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Apparatus for study of adsorption of vapors on mercury

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APPARATUS FOR STUDY OF ADSORPTION OF VAPORS ON MERCURY

by

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I. INTRODUCTION

The primary purpose of this project was to devise a method for obtaining data on the adsorption of vapors on a mercury surface. One of the complicating factors that makes the formation of a quantitative theory of adsorption difficult is the supposed heterogeneity of the surfaces of the adsorbent used. If an adsorbent with a uniform, homogeneous, and reproducible surface could be used to study adsorption, this difficulty would be removed.

For this reason mercury was chosen as the adsorbent since it should have a homogeneous, reproducible surface. Other advantages of mercury as an adsorbent are (a) it has a high surface tension and thus should approximate a solid surface with respect to adsorption; (b) adsorption on the mercury surface can be followed by means of surface tension measurements, the adsorption being calculated by means of the Gibbs adsorption equation; (c) although mercury is difficult to purify completely and to keep pure (as are all adsorbents), its purity can be determined by the same surface tension measurements used to measure adsorption; (d) it is readily available and can be distilled under vacuum with little difficulty.

There are several methods available for the determination of surface tension. For this work it was desirable to choose a method which was static in nature, suitable for use in vacuum, and of a high degree of precision and accuracy. It was felt that the recently developed pendent drop method best met these requirements.

The purposes of this research, then, were as follows:

1. To design and build an apparatus that could be used to determine the surface tension of mercury in high vacuum under conditions of maximum purity, and to demonstrate the practicality of the apparatus.

2. To measure the surface tension of pure mercury and compare the value obtained with the presently accepted value.

3. To obtain adsorption isotherms for n-heptane and ethanol, both singly and from mixtures of the two vapors, by observing the dependence of the surface tension lowering of mercury on the partial pressures of these vapors.

4. To find a theoretical expression which would represent the data so obtained.

II. LITERATURE

A. Surface Tension of Mercury

Many workers have tried to determine the value of the surface tension of mercury. One of the earliest determinations was made in 1831 by Poisson (32) who obtained a value of 442 dynes/cm using a drop method. Since that time values ranging from 430 to 515 dynes/cm have been found by various workers using a variety of methods such as drop weight, bubble pressure, capillary rise, and sessile drop. In an article published in 1936, Puls (33) included a table of 25 values for the surface tension of mercury together with the method used and a reference to the original article in each case. Since several critical discussions of these various and varying values are available (1, 13, 23), a detailed discussion will not be given here. In general, the discrepancies were attributed to contamination of the mercury, although in some cases the application of the particular method used cast doubt on the accuracy of the results.

In 1932, Burdon (13) reported a value of 488 dynes/cm in vacuum by the method of the large sessile drop. He also presented a good critical discussion of the data to that time. In 1938, Bosworth (10) reported 484 dynes/cm at 20° C in purified and dried air using the maximum bubble pressure method. By observation of mercury sealed in a tube, Bate (9) obtained a value of 490 dynes/cm at 20° C in vacuum.

Probably the best and most careful determination reported to date was that of Kemball (23). Using the method of the sessile drop, he obtained a value of 484 $\pm$ 1.5 dynes/cm at 25° C in vacuum. Kemball used carefully purified mercury and analyzed all possible sources of error due to the apparatus used. He also reviewed values found by other workers and discussed in particular the higher values that have been obtained. (Three values higher than 488 dynes/cm have been reported since 1900 (11, 15, 35).) He felt that the error in two of these cases may have been caused by the window used in the sessile drop apparatus. In the third case (35), the theory of the method (stationary waves on a vertical jet) could not be regarded as accurate.

In a book published in 1949, Burdon (14) discussed the surface tension of mercury and the discordance in values and concluded that the value for the surface tension of mercury lay within 1 percent of 485 dynes/cm. He included a list of some of the more recent values for the surface tension of mercury in vacuum and in various gases. Adam (1) listed the value of the surface tension of mercury as 485 $\pm$ 5 dynes/cm.

It appears, then, that the surface tension of pure mercury is probably very close to the value found by Kemball, i.e., 484 dynes/cm. This value can be attained only with great difficulty, however. The mercury must be very pure since even small amounts of impurities can lower the surface tension considerably. While it is a relatively simple matter to obtain mercury of reasonably high purity, the purity demanded for surface tension work seems to require rather elaborate purification procedures. In addition, all surfaces with which the

mercury comes into contact must be scrupulously clean and completely inert with respect to the mercury. Although there were differences of opinion about the actual value of the surface tension of mercury, there was general agreement that the temperature coefficient of the surface tension is 0.20-0.23 dynes/cm/degree.

B. Adsorption of Vapors on Mercury

Although a number of papers have been published over a period of years on adsorption of various vapors on mercury, the results reported are subject to the same criticisms as are those for the surface tension of mercury since adsorption on a liquid surface was most often determined by lowering of surface tension. Contamination of the mercury surface and errors in measurements made the results of only qualitative value. Some of these results were discussed by Adam (1) and also by Kemball and Rideal (24). There was considerable lowering of the surface tension of mercury (as determined by each worker) by organic vapors in all cases. This additional lowering of the surface tension indicated that these vapors may have displaced the layer of contamination originally present. Adam concluded that one could not say much more from the results found except that the adsorbed films of organic vapors on mercury are usually gaseous and that there may be more lateral adhesion in the films of short chain polar substances than in films of hydrocarbons.

Probably the most reliable data on the adsorption of vapors on mercury were obtained by Kemball and Rideal (24) and by Kemball (25), (26). Adsorption of both polar and non-polar vapors was studied. In

the case of non-polar vapors, reversible results were obtained for the adsorption of benzene, toluene, and n-heptane. The films were found to be gaseous and to obey the Volmer equation for a gaseous surface film,

$$\pi (A-b) = kT \quad \text{where} \tag{1}$$

π = spreading pressure

A = area per molecule

b = co-area.

Experimental co-areas at low pressures for both benzene and toluene indicated that in each case monolayers were formed with the molecules lying flat on the surface. In the case of n-heptane, experimental results indicated that the molecules were partially curled up with 4 or 5 carbon atoms in contact with the mercury surface. The reversibility of adsorption and the magnitude of the heat of adsorption in all these cases indicated that only van der Waals interactions were present. At higher pressures further adsorption of n-heptane occurred with either the formation of a second layer or two-dimensional condensation in the first layer. Results for toluene indicated two phase changes; the first involving a change from adsorption flat on the surface to end-on adsorption and the second probably representing the formation of a second layer.

Reversible adsorption was also found for the polar substances, water, acetone, and the normal alcohols from methyl to hexyl. All these substances except water formed gaseous films at low pressures. The Volmer equation was applied in every case with satisfactory results. (However, see Discussion, p. 59). The Langmuir equation,

which is based on the assumption of adsorption to fixed sites, was applied to the data for water giving slightly better results than did the Volmer equation. The large entropy of adsorption for water indicated that the molecules might be immobile on the surface. This high entropy also strongly indicated the association of water on the surface of the mercury. There was probably some association of methyl alcohol, also. N-Butyl, n-amyl, and n-hexyl alcohols formed gaseous films with the molecules flat on the surface. End-on adsorption probably occurred in the case of acetone. Methyl and ethyl alcohols formed second layers while the higher alcohols formed condensed films. Propyl alcohol exhibited behavior between the two. Water showed no inclination to form a second layer.

C. Pendent Drop Method

Since the pendent drop method of measuring surface tension is relatively new and as yet is not widely used, a discussion of the method, of some of its uses, and of its development to the present time seems appropriate.

The pendent drop method in its present form was developed by Andreas, Hauser, and Tucker and reported in 1938 (3). The background of the method is adequately discussed in their paper. Andreas *et al.* designed an apparatus in which a small drop of liquid could be suspended from the end of a vertical tube and then photographed. They further developed a method for calculating surface tension from the size and shape of the drop. A discussion of this method follows.

1. Theory

The mathematical treatment of a pendent drop is based on two fundamental equations. The first states that the pressure caused by curvature of a surface is equal to the product of the surface tension and the mean curvature.

$$P = \gamma\left(\frac{1}{R} + \frac{1}{R'}\right) \qquad (2)$$

The second states that when the drop is in equilibrium, the vertical forces acting across any horizontal plane are balanced.

$$2\pi x \gamma \sin \phi = V \sigma g + \pi x^2 P \qquad (3)$$

P = pressure due to curvature of the surface

R and R' = two principal radii of curvature

x = horizontal distance to axis of drop

ϕ = angle between normal and axis

V = volume of fluid hanging from plane

σ = difference in density

γ = surface tension

g = acceleration of gravity (see Figure 1).

These equations may be combined in various ways to obtain a differential equation of the drop and a method of determining the surface tension. Andreas, Hauser and Tucker rejected the method of the plane of inflection, which had previously been tried, because finding the exact location of the true plane of inflection presented a difficult graphical problem and because it was necessary to compute the volume of the drop from its profile, again a tedious and difficult procedure. They developed instead the method of the selected plane.

In order to do this, they first determined the differential equation of the drop by eliminating R + R' and combining equations 1 and 2.

$$\frac{d^2z}{dx^2} + \frac{\frac{dz}{dx}}{x}\left[1 + \left(\frac{dz}{dx}\right)^2\right] = \left[\frac{2}{b} - \frac{g\rho^2}{\gamma}\right]\left[1 + \left(\frac{dz}{dx}\right)^2\right]^{3/2} \qquad (4)$$

z = vertical coordinate measured away from the origin, taken at the bottom of the drop (where the axis of rotation cuts the surface of the drop).

b = radius of curvature at the origin.

The size of the drop is most conveniently determined by measuring the diameter at the equator (i.e., the greatest horizontal diameter), and the shape is described by giving the ratio of diameters measured at two different horizontal planes. The two planes chosen were the plane of the equator, giving the equatorial diameter, d_e, and the plane a distance from the tip of the drop equal to the diameter at the equator, giving the diameter, d_s. (See Figure 1) The shape was then described as $S = \frac{d_s}{d_e}$.

By making appropriate substitutions, the authors arrived finally at the equation

$$\gamma = \frac{g\rho(d_e)^2}{H} \qquad (5)$$

where H is a function of S and can be determined from the differential equation of the drop. With a table of H as a function of S, the surface tension can be determined. Andreas et al. stated that the equation is exact and convenient and that the precision depends only upon the accuracy with which the linear measurements can be made and upon the tables of H vs S.

These workers felt that although it was theoretically possible

to evaluate the function (H) mathematically, the calculations would be very laborious and unsatisfactory. Therefore, they established an empirical table from measurements on photographs of various sized drops of conductivity water of known surface tension. They felt that if linear dimensions could be measured with a probable error of not more than $\pm$ 0.1 percent, the surface tension could be measured with an uncertainty of about $\pm$ 0.5 percent.

A sketch of the apparatus used by Andreas, Hauser, and Tucker is shown in Figure 2. Drop forming tips were made of 2 mm pyrex tubing and sealed onto 1.5 cc hypodermic syringes. The drop was formed inside a glass cuvette which was enclosed in a water thermostat. The light source consisted of a mercury arc lamp and a condensing lens. The camera was fitted with a microscope objective and telecentric stop.

Surface tensions of 10-second-old surfaces of benzene, ethanol, methanol, and toluene were determined. The agreement with literature was good. Interfacial tensions of mercury-benzene, mercury-water, water-benzene, water-carbon tetrachloride, and water-toluene systems were also determined. In these cases the agreement with literature was not quite so good as was the case with surface tensions. The authors stated that published values of interfacial tensions were frequently of low precision. Also, all of their measurements were on 10-second-old surfaces whereas the age of surfaces for the previously published values was unknown. They believed their errors for interfacial tensions to be within $\pm$ 1 percent. They found that results were independent of whether the drop was pendent up or pendent down. (A drop hanging

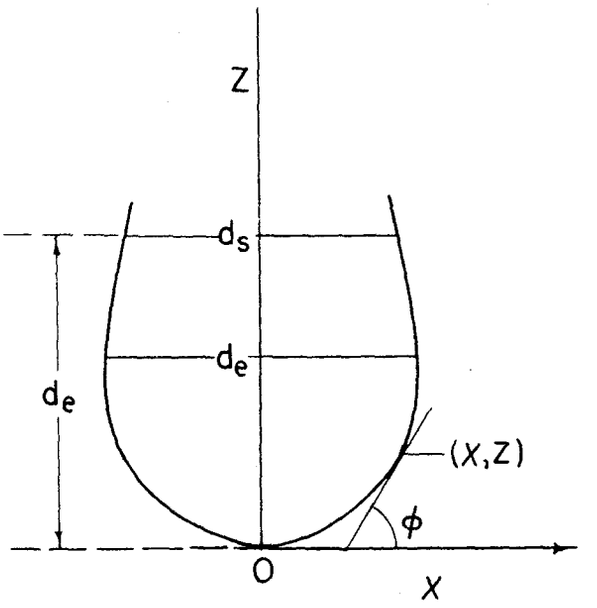

FIGURE 1. THE PENDENT DROP

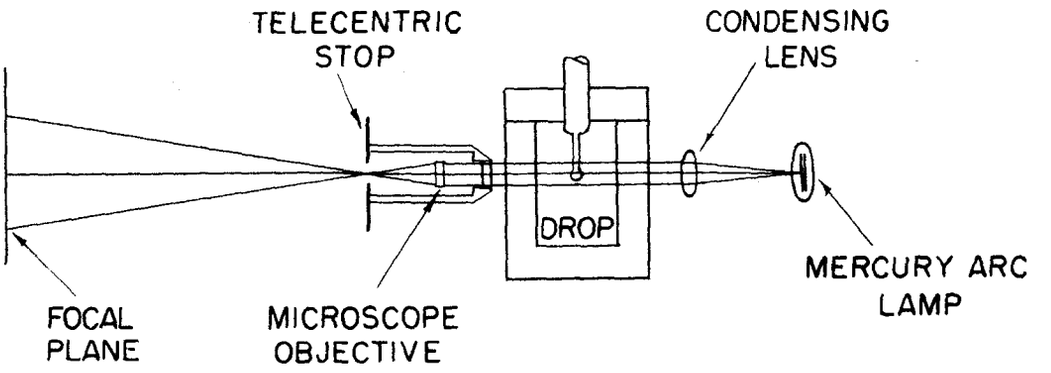

FIGURE 2. APPARATUS OF ANDREAS, HAUSER & TUCKER

downward from a drop forming tip is referred to as "pendent down". In some cases, it may be desirable to form the drop upward from a drop-forming tip, or "pendent up".) While they claimed an accuracy of $\pm$ 0.5 percent for surface tensions, they believed that the method was capable of an accuracy of $\pm$ 0.05 percent.

Andreas, Hauser, and Tucker listed the outstanding advantages of the pendent drop method as

1) complete mathematical analysis
2) results independent of contact angle between the fluid interface and the apparatus
3) method is static and therefore not influenced by viscosity effects
4) measurements are made instantaneously
5) successive measurements of a given surface can be made without disturbing it
6) boundary tensions of any magnitude can be observed
7) either surface tension or interfacial tension can be measured in any system in which at least one of the fluids is transparent and the fluids are not of equal density
8) only small samples are required
9) adapted to simple temperature control
10) photographs on which measurements are made may serve as a permanent record.

2. Development of apparatus

Naturally, the original pendent drop apparatus was improved as it was used. For the most part these improvements consisted not of

drastic changes but of improvement of various sections of the apparatus. Mack, Davis, and Bartell (27) placed the tip in a pyrex cell with optically flat windows. Smith (36) used a better lens and a camera arrangement which gave constant magnification. He also mounted a glass syringe with special drop-forming tip on a microscope mechanical stage. Drops were expelled with the aid of a screw which acted upon the plunger and pictures were measured with the aid of a special microscope mechanical stage fitted with vernier which could be read directly to 0.05 mm. This apparatus gave higher precision and greater convenience and speed of operation than those used before. The mercury arc lamp originally used as the light source gave way to the recently developed concentrated arc light source (12) (Hauser and Michaels (22) and Bartell and Bard (5)).

In 1948, Hauser and Michaels reported a pendent drop apparatus for liquid-liquid systems in the temperature range, 20°-200° C and a pressure range of 0-10,000 pounds/square inch. Measurements were made with an engraved rule and hand magnifier to 0.1 mm. Magnification was determined from the known diameter of the drop-forming tip.

3. Extension of theory

In 1944, Smith (36) had mentioned the need for the refinement of the H-S tables.

The first set of theoretical tables for H as a function of S was published in 1948 by Fordham (18). A short time later a similar table was published by Niederhauser and Bartell (31). The two tables checked one another very closely. Both sets of tables gave 1/H as a

function of S. The accuracy of Fordham's tables was given as

S = 0.60 - 0.68	max. error	± 0.00003	= ± 0.003%
S = 0.68 - 0.98	" "	± 0.00001	= ± 0.001% - 0.003%
S = 0.98 - 1.00	" "	± 0.00003	= ± 0.01%.

Fordham considered the agreement between these tables and the experimental tables of Andreas, Hauser, and Tucker to be satisfactory. He believed the method should be capable of giving results as reliable as those for capillary elevations. However, the "attainment of such accuracy would entail very stringent demands upon experimental techniques". The errors in the Niederhauser and Bartell table of 1/H vs S were claimed to be not greater than one unit in the fifth decimal place for S less than 0.985 and not more than three units for S = 0.985 - 1.002. These authors stated that "as a result of this evaluation the pendent drop method is probably the most accurate of known methods, as well as an absolute method, for measuring boundary tensions".

4. Applications

Smith and Sorg (37) and Smith (36) used the pendent drop method to determine the surface tensions of organic liquids. Smith and Sorg measured surface tensions of alcohols ranging from C_1 to C_{12}. They attributed values that were higher than literature values to purer liquids. The surfaces which they photographed were 10 seconds old. Smith determined surface tensions of 15 highly purified hydrocarbons in the range C_5 to C_8. He felt that his precision was that of the empirical H-S tables then available.

Several workers applied the method to interfacial tensions.

Bartell and Davis (6) studied the interfacial tensions of water-air, water-n-heptane, water-benzene, and water-methyl n-amyl ketone systems. Bartell and Niederhauser (8) used the pendent drop method to measure interfacial tensions of crude petroleum oils with water. Using an aluminum mirror and a ruled glass plate, they could make measurements directly to 0.2 mm in about one minute. For greater accuracy, they employed the photographic method which took about 20 minutes and was accurate to about 1 percent. Bartell and Bard (5) studied mercury-water and mercury-organic liquid systems in the presence of various atmospheric gases. They claimed an absolute accuracy of 0.2 percent.

Mathews (28) utilized the pendent drop method to study oil in glue interfacial tensions. In this case the method was chosen, not because any great accuracy was desired, but because this method could be used for the system under study whereas other methods could not be so used.

A study of the interfacial tensions of sodium laurate solutions against heptane and against air was made by Bartell and Davis (7).

Addison and Hutchinson (2) applied a modification of the pendent drop method along with other methods to a study of the surfaces of aqueous decyl alcohol solutions. They formed a drop of known volume on an orifice, illuminated it from behind, and observed its length with a microscope carrying an eyepiece scale. A calibration curve for drop length and surface tension was obtained from a series of solutions of known surface tensions. Thus time-surface tension curves could be obtained directly from the movement of the drop perimeter over the

eyepiece scale. Values so obtained agreed with those obtained by a drop weight method but were higher than those obtained from a vertical plate method. The authors felt that the vertical plate method gave the true surface tension values and that the hanging drop gave apparent surface tension values due to a "bag" formed around the drop by lateral adhesion in an adsorbed film which acted as an additional upward force on the drop. This appears to be a rather unusual explanation since the nature of surface tension as usually conceived does not permit lateral adhesion of molecules to be considered independently. The reason for these discrepancies in surface tension measurements is not clear. However, the vertical plate method is not completely a static method whereas the pendent drop method is. The explanation may lie in this difference.

In 1941, Mack, Davis, and Bartell (27) reported the use of the pendent drop method to determine the surface tension of gallium. Oxygen and water vapor were excluded and the surface tension measured under an atmosphere of hydrogen and of carbon dioxide. The value which they found for the surface tension of gallium near its melting point (30° C) was 735 ± 29 dynes/cm. Richards and Boyer (34) had much earlier (1921) reported a value of 358.2 dynes/cm for the surface tension of gallium at 30° C. These latter authors obtained a value of 432 dynes/cm for the surface tension of mercury using the same method, the method of the large drop. One might well expect the surface tension of gallium to be higher than that of mercury and that gallium would be even more difficult to obtain in a pure state. It

would not be surprising, then, if early values for the surface tension of gallium as for the surface tension of mercury were quite low. The value found by Mack, Davis, and Bartell may be near the correct value.

Davis and Bartell (16) applied the pendent drop method to molten materials. In order to apply their method, they assumed that the shape of the molten drop did not change upon cooling although the volume and density did change. This assumption appeared to be justified in the case of isotropic substances. Their procedure was to heat a small amount of solid or viscous material until it melted or flowed sufficiently to form a pendent drop. The drop was then allowed to solidify, and its linear dimensions were measured at room temperature. The drop itself served as a permanent record. Equation 5 was revised to fit this case. D_e, D_s, and $\sum$ are the measured room temperature values corresponding to d_e, d_s, and σ. For isotropic substances, the third power of the linear diameter is proportional to the volume; the density is inversely proportional to the volume. Therefore

$$\left(\frac{de}{D_e}\right)^3 = \frac{\sum}{\sigma}$$

The equation then becomes

$$\gamma = \sum^{2/3} \sigma^{1/3} g D_e^2 \frac{1}{H} . \qquad (6)$$

This method was used for glasses, waxes, polystyrene, electrolytic iron, lead oxide, antimony trioxide, and lead chloride. The glasses and waxes gave values which agreed with the literature values. The

value found for electrolytic iron was 840 dynes/cm. The literature value given for the surface tension of gray cast iron is 880 dynes/cm (1). It is quite possible that these values are both much lower than the true value of the surface tension of iron. The limits of accuracy of this method for molten materials can be determined only by further study.

In 1951, Michaels and Hauser (30) reported some results obtained from their high pressure apparatus which is described on page 12. They studied the benzene-water and n-decane-water systems over a pressure range of 700 atmospheres and at temperatures ranging from 20°-130° C. Before calculating surface tension values, they rewrote equation (5) as $\frac{\gamma}{\sigma g} = \frac{d_e^2}{H}$ of which $\frac{d_e^2}{H}$ was obtained experimentally. This value was then plotted as a function of pressure and temperature and the data "smoothed out" before the additional inaccuracies of density values given in the literature were introduced.

To summarize, the pendent drop method has been used to study both surface and interfacial tensions. It has been applied to materials ranging from organic liquids to molten iron. While most of the work has been carried out at normal temperatures and pressures, the method has been applied over a pressure range of 700 atmospheres and at temperatures as high as 130° C. With the exception of Addison and Hutchinson, those who have worked with the pendent drop method seem to agree that it is an exact, accurate method for the determination of boundary tension. Some, such as Douglas (17), have urged its wider

use as a convenient, accurate, and fundamental method for the evaluation of boundary tensions and of related phenomena. The advantages claimed for the method by those who developed it seem justified.

It is to be noted, however, that none of the reports so far published mentioned a use of the method in vacuum. It seemed that it should be possible to adapt the method to vacuum and thus increase its usefulness even further by making it possible to determine surface tensions under optimum conditions.

III. APPARATUS

The apparatus for the pendent drop method as carried out in this study can conveniently be divided into (1) the optical system, (2) the vacuum system, (3) the vapor inlet system, (4) vibration support and mounting, (5) temperature control, and (6) measuring machine. Each of these will be discussed in detail.

A. Optical System

The optical system for the pendent drop apparatus is essentially a system for profile projection. The necessary elements for such a system are

1. an illuminating system, i.e., a light source and a condensing lens,
2. a suitable fixture to carry the object to be projected,
3. a projection lens, and
4. a screen and/or photographic plate to receive the image.

1. Equipment

In profile projection light from the source illuminates the object, passes through the projection lens, and casts an image of the object upon the screen or photographic plate. This image should be a sharp, faithful and undistorted reproduction of the object.

The illuminating system used in this work was a "zirconarc" lamp which utilized the "concentrated arc" light source (12). The

concentrated arc bulb (40 watt) produced a high intensity light source in the form of a circular spot 0.037 inches in diameter. It therefore approached a point source. The condenser system of the "zirconarc" lamp was reportedly well corrected for spherical aberration, coma, and color. The exact meaning of "well corrected" could not be determined. The equivalent focal length was 16.5 mm.

The shutter for the system was placed on the lamp rather than on the camera. This arrangement decreased vibration and prevented excessive heating of the object by the light source. A multilayer mercury green light filter was obtained to provide monochromatic light. It was found, however, that there was not sufficient difference in definition of the image with the use of this filter to counteract the disadvantage of the longer exposure time necessary. For this reason the filter was not used.

A 35 mm/f/2.3 Baltar lens was used as a projection lens. A 32 mm micro-tessar lens was also tried but the Baltar was found to be more satisfactory from the standpoint of aperture, magnification, and freedom from distortion.

The Baltar lenses were reported to "have extreme flatness of field, high resolving power, and [to be] well corrected for all aberrations."[1] Once again it was impossible to obtain information about how well the lens was corrected.

The object whose image was to be projected was a drop of mercury

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[1]Letter from Frank Hawkins, Photographic Sales Dept., Bausch & Lomb, 1950.

hanging from a glass tip within a cell bounded by two parallel, optically flat windows (Figure 3). The outside diameter of the drop-forming tip was about 4 mm while the inside diameter was about 2 mm. The maximum diameter of the mercury drop was about 3 mm. The nature of the drop was such as to offer no particular difficulties in its projection. An absorption cell of the following specifications was used as the cell within which the drop was formed.

Parallelism of liquid-glass interfaces	0.01 mm
Flatness of windows	6 wavelengths
Parallelism of faces of each window	within 5 minutes.

The camera designed for use with this system consisted of lens, focusing device, bellows, and a holder for a ground glass screen and the photographic plates. The image was first focused on the ground glass plate. Before a photograph was taken, this plate was removed and a loaded plate holder was inserted in the same position. A plumb line consisting of a lead drop attached to a nylon thread was fastened to the camera in front of the photographic plate so that its shadow was cast on the exposed plate where it served as a reference line for alignment of the photograph on the measuring machine.

The camera, as built, was not completely satisfactory. It was not sufficiently rigid and neither the lens nor the plate receiver was properly squared to the optical axis. Consequently, alignment with the light source and with the cell was difficult and frequent realignment was necessary.

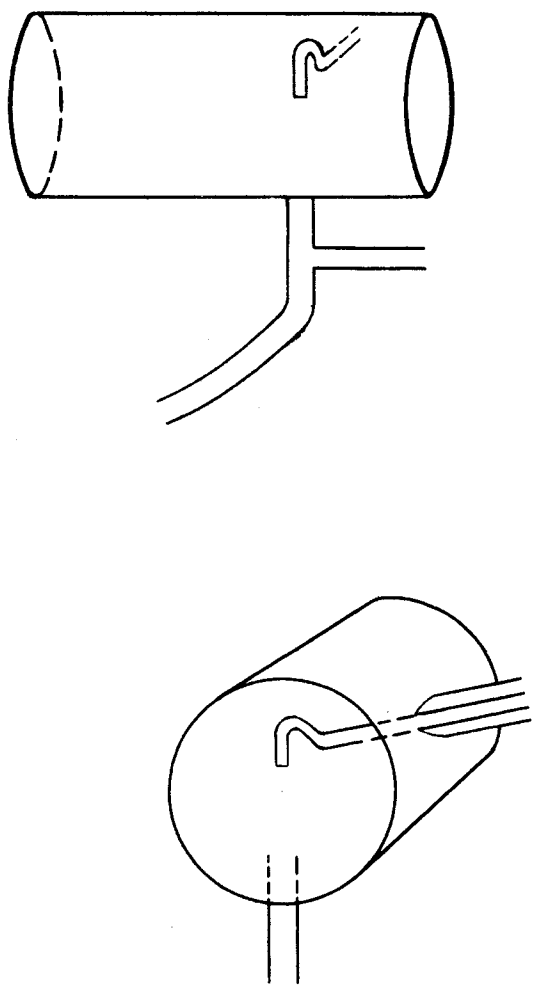

FIGURE 3. CELL AND DROP FORMING TIP. ABOVE, SIDE VIEW; BELOW, END VIEW.

Both the camera and the light source were fitted with rollers which rode upon a sturdy optical bench. The light source could be moved to any desired position while the camera could be moved as a unit or the front rollers could be clamped into position and only the back rollers moved to provide extension or compression of the bellows. The optical bench could be raised, lowered, and leveled by means of screws attached to each of the four feet.

Kodak spectroscopic M plates, 649-GH plates, and 548-GH plates (later called High Resolution Plates) were all used from time to time. The M plates, while very fast, had low resolving power and were unsuitable for this work. The highest resolving power (1000 lines per millimeter) was obtained with the 649-GH plates. These plates also required the longest exposure time, about 45 seconds without a filter at the magnification used. The High Resolution Plates required about 10 seconds exposure without the filter. Resolving power of these latter plates seemed quite satisfactory, inasmuch as a well-focused image appeared sharp and clear under the traveling microscope of the measuring machine. These plates, therefore, were finally adopted for use in this study.

The camera, cell, and light source were aligned as well as possible in the following manner. The camera and light source were aligned by adjusting them so that the light from the light source entered the center of the projection lens and formed a circular spot on a ground glass screen at the back of the camera. This circular spot became uniformly smaller and larger as the apertures of the projection and condensing lenses were closed and opened if alignment was good. The

optical bench was then adjusted so that light from the light source fell on the cell window and was reflected back to the center of the light source lens while, at the same time, the image of the drop-forming tip fell in the proper position on the ground glass plate.

2. Sources of error

Possible sources of error from this optical system included distortion caused by the projection lens, any optical imperfections in the cell windows, non-alignment of the various components of the system, and uncertainties caused by the nature of light and of the photographic process. Sources of error such as improper focusing and vibration of the drop were, of course, immediately obvious on the photograph.

About the only way to determine the extent of distortion of the lens was to photograph an object of known size and to determine the extent of any distortion in the image of this object. Several pictures of micrometer discs taped to the window nearer the projection lens were taken. One of the micrometer discs was ruled in squares 0.25 mm in area; the other disc was linear, 5 mm long with rulings each 0.1 mm. Measurement of these photographs indicated a rather significant pin-cushion distortion. However, comparison of a drop photograph with the squared micrometer disc photographs indicated that the corrections were such as almost to cancel one another. Both the tip diameter and d_e as measured on the photograph were too large due to the distortion effect, but about the same correction would have been applied to both values so that the actual value of d_e^2 (d_e measured X actual tip diameter/tip diameter measured) remained unaltered (See

Figure 4). The distance from the tip of the drop to the plane of d_s was similarly too large, since the measured d_e was too large and the drop was somewhat extended in this region due to the distortion effect. This gave an apparent low value for d_s. However, if d_s had been measured in the corrected plane (dotted line in Figure 4) and corrected for horizontal distortion, approximately the measured value would have been obtained. Hence the two corrections on d_s approximately cancelled one another. The value of d_s/d_e, on the other hand, was still too small since the measured d_e was too large by a greater fraction than that of d_s. This might have led to a high value for the surface tension. The resultant error, though, was probably no greater than the uncertainty in measurement, i.e., error in surface tension caused by this effect was probably of the order of 1 dyne/cm or less.

Considering the discussion of Kemball (23), the specifications of the cells used, and the size of the object, any error due to the cell windows should have been negligible.

Uncertainties caused by non-alignment of the various components of the optical system could have been serious. If the parts were not aligned as well as they should have been, it was impossible to focus the image properly. Part or all of the photograph then had a fuzzy appearance and it was often difficult or impossible to decide where the measurements should be taken. This effect could cause a difference in surface tension values of as much as 2 dynes/cm or 0.4-0.5 percent.

In profile projection there might be some undertainty as to which part of the object the image corresponds. That is, the light might image a plane other than the plane of maximum diameter if the object

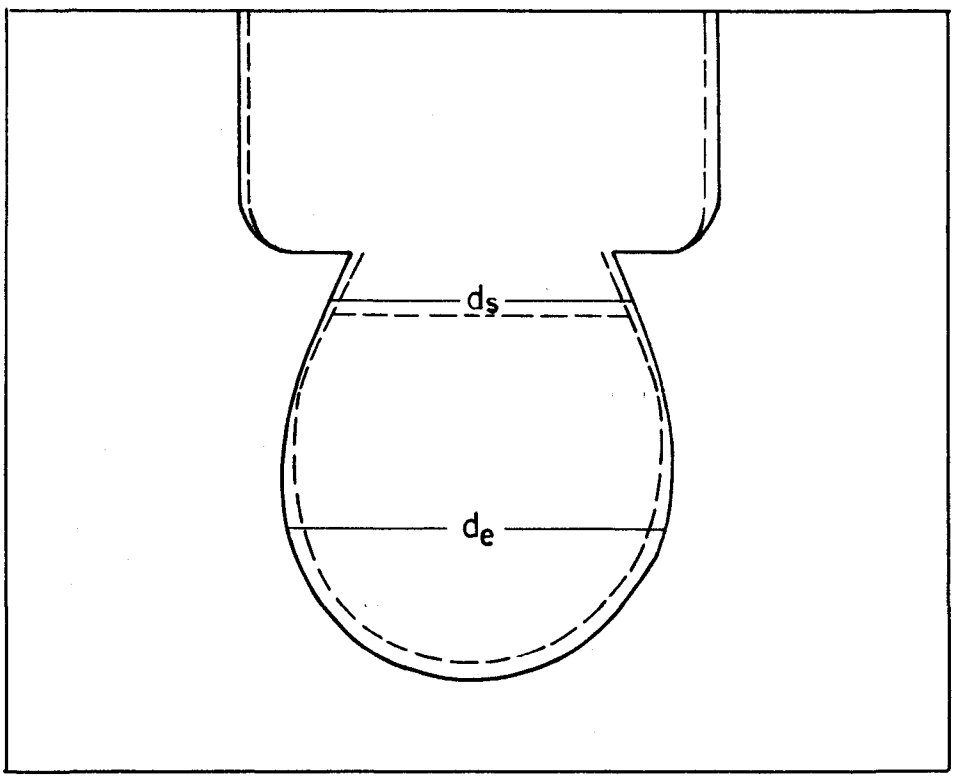

FIGURE 4. DROP PHOTOGRAPH AS RELATED TO POSSIBLE LENS DISTORTION. DOTTED LINES INDICATE PROBABLE IMAGE OF DROP (GREATLY EXAGGERATED) IF NO DISTORTION WERE PRESENT.

is on the optical axis. If the object is off the optical axis, the image would be distorted (See Figure 5a). These difficulties are removed when collimated light is used as shown in Figure 5b (See Habell and Cox (21)). The illumination used in these measurements was nearly parallel. The angle θ (Figure 5a) was 2 arc sin .47/16.5 (diameter of light source = .94 mm; focal length = 16.5 mm), and the s/f ratio was approximately that recommended by Habell and Cox (s = source diameter; f = focal length).

The diffraction of light is another effect which causes uncertainty when measurements to a high degree of precision are desired. The theory for diffraction about a surface seems to be not at all worked out and so it is difficult to predict the magnitude of this effect. When this system was aligned well and properly focused and exposed, a very sharp photograph with no evidence of diffraction lines was obtained. If these conditions were met, and it was all too obvious when they were not, it was felt that the uncertainty due to this diffraction effect was very small, especially since no absolute measurements of the drop, but only ratios of measurements, were used.

Measurements of the dropping tip by direct measurement and by the photographic method indicated that the optical system as described did not produce large errors. The dropping tip was measured directly with the measuring machine before being sealed into the system. The value obtained from 40 measurements was 3.825 ± 0.006 mm (absolute deviation). Later, Mr. Lyle Nesbitt measured the same tip by inserting calibrated steel balls into the cell just below the tip,

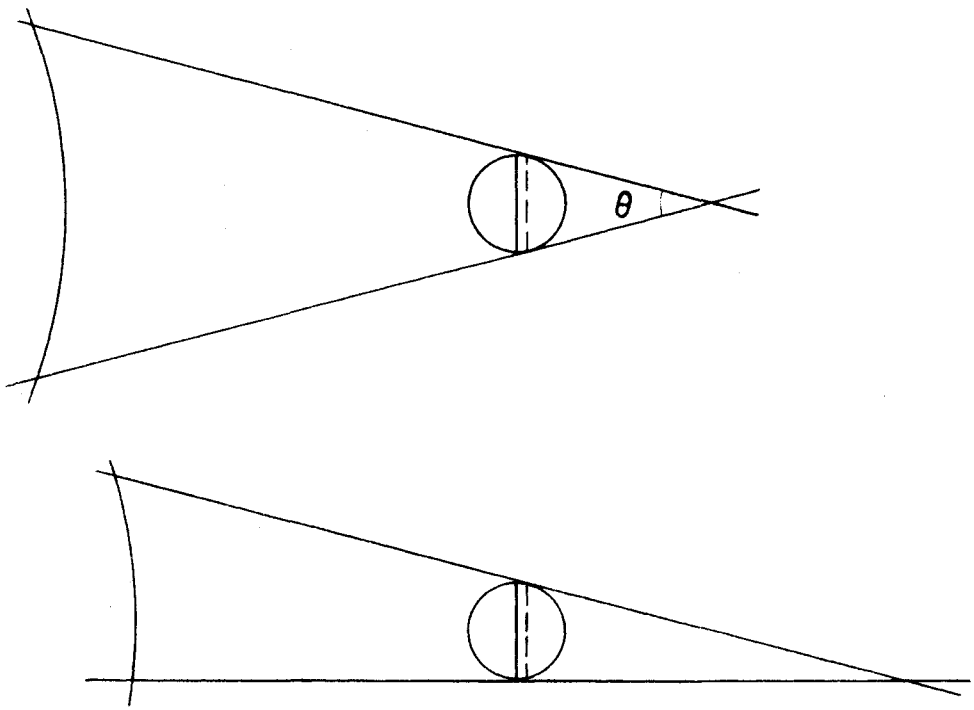

FIGURE 5a. EFFECT OF CONVERGENT LIGHT ON PROJECTION OF SPHERICAL OBJECT. ABOVE, AN OPTICAL AXIS; BELOW, OFF OPTICAL AXIS

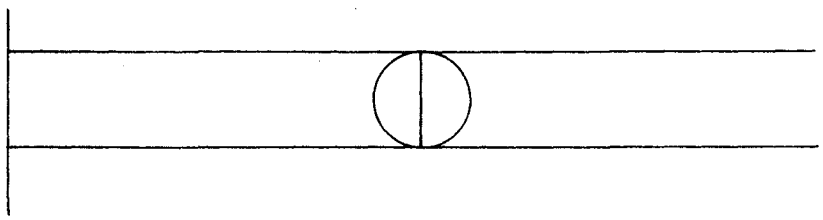

FIGURE 5b. EFFECT OF COLLIMATED LIGHT ON PROJECTION OF SPHERICAL OBJECT

photographing the tip and ball, and determining the tip diameter from measurements of the photographs. He obtained a value of 3.829 mm. This represents a difference of only about 0.1 percent.

B. Vacuum System

Any vacuum system for adsorption of vapors on mercury by a pendent drop method must include (1) vacuum pumps and gages, (2) a method of introducing pure mercury into the system, preferably by distillation, (3) a method of controlling the flow of mercury and of controlling the size of the mercury drop, (4) a cell with dropping tip, (5) a vapor inlet system, and (6) a method of measuring the pressure of the vapor.

Several problems presented themselves when a design for a vacuum system such as this was considered. One of the most fundamental problems which made the solution of other problems more difficult was the necessity of using no material in the vicinity of the mercury which had any significant vapor pressure. Kemball (23) found that stopcock grease, even though it had very low vapor pressure, could not be used because of slow diffusion and subsequent adsorption on the mercury surface. Consequently, it was necessary to find substitutes for the usual grease-lubricated stopcocks. This was not a simple task. This problem was important in the drop control system, and in the vapor inlet system, as well as in making connections between the cell area and the manifold. Solutions to this problem will be indicated under the various sections.

1. Vacuum pumps and gages

A Welch Duo-seal forepump was used in connection with an H. S. Martin and Company single stage diffusion pump. With these two pumps, it was possible to obtain pressures as low as 10^{-5} mm Hg readily and $4\text{-}5 \times 10^{-6}$ mm Hg under optimum conditions. Pressures were indicated by a National Research Corporation vacuum thermocouple gage and an ion gage.

2. Mercury distillation and mercury reservoir

Mercury was introduced into the system through a still with a vertical water condenser as indicated in Figure 6. At first this mercury ran from the still directly to a mercury reservoir and thence to the drop control and the cell. Mercury obtained in this manner appeared to be insufficiently pure. Cyclic distillation is generally believed to improve the purity of substances. Hence provision for cyclic distillation was made. A second still was introduced in such a manner that mercury passed from the cell to this secondary still from which it could be redistilled into a tube leading to the mercury reservoir, thus permitting the distillation to be continued as long as desired. Still later this section was modified so that the mercury from the first still ran directly into the secondary still from which it was distilled into the mercury reservoir (Figure 6). Any impurities that might possibly have entered the system from the first still were thus trapped in the second still and could not reach the drop control. This arrangement appeared to be quite satisfactory. It was also possible with this arrangement to seal off the first still after a sufficient

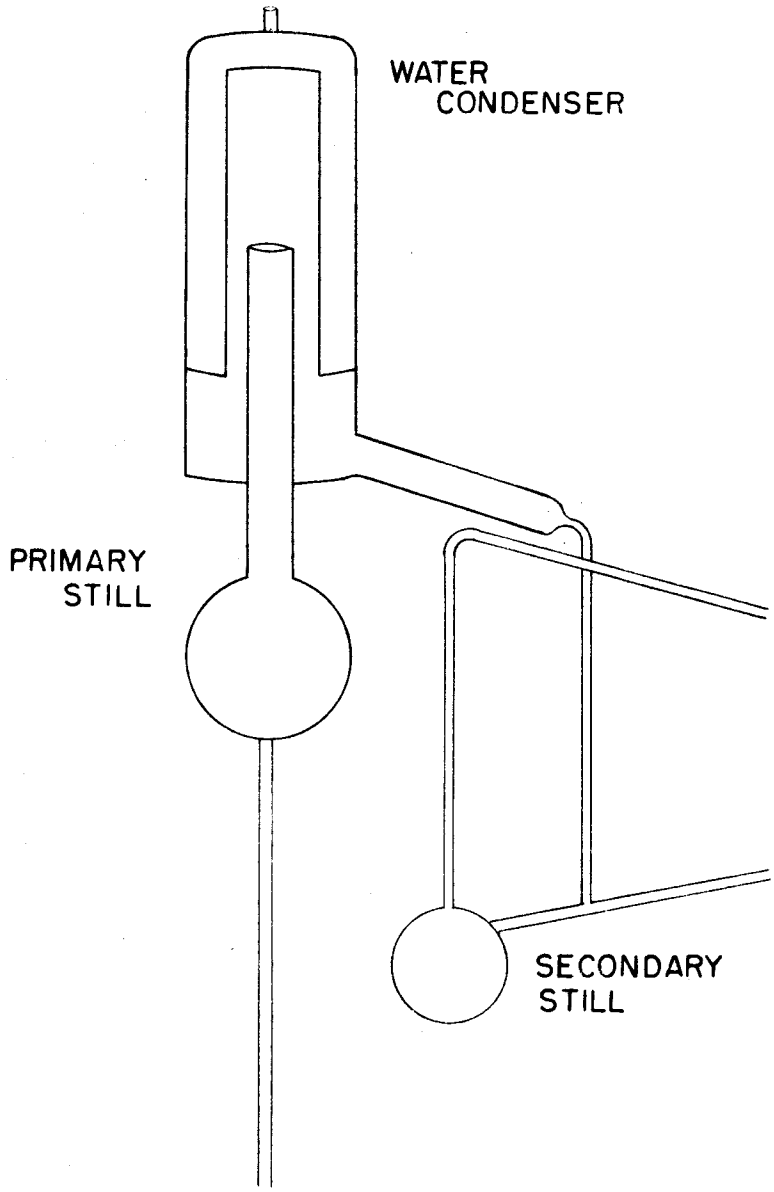

FIGURE 6. MERCURY STILLS

amount of mercury had been distilled into the second still, if desired.

The purpose of the mercury reservoir was to store pure mercury ready for use in the drop control. The reservoir consisted simply of a piece of glass tubing of large diameter. This was first connected to the vacuum system through an ordinary vacuum stopcock and a liquid air trap to remove any vapors from the stopcock grease. Later it was completely disconnected from the vacuum manifold in order to eliminate the stopcock and the trap. This part of the system could then be evacuated through the cell but only if the connecting tubes were not sealed with mercury. This proved to be quite unsatisfactory, especially when adsorption studies were made. Finally, the reservoir was connected to the vacuum manifold directly without the use of a stopcock of any kind (Figure 11).

3. Drop control

Early attempts to control the flow of mercury involved the use of a teflon plug ground to fit the barrel of a glass stopcock, in the hope that this might be self-lubricating and vacuum tight. Although several such stopcocks were ground, none of them could be made vacuum tight, even with mercury seals. Accordingly, this procedure was abandoned. A design which could control the flow of mercury and at the same time control the size of the drop was adopted. This consisted of a plunger which fit fairly snugly within a barrel to which a side arm was attached (Figure 7). When the plunger was above the side arm, mercury could flow from this side arm into the barrel; when the

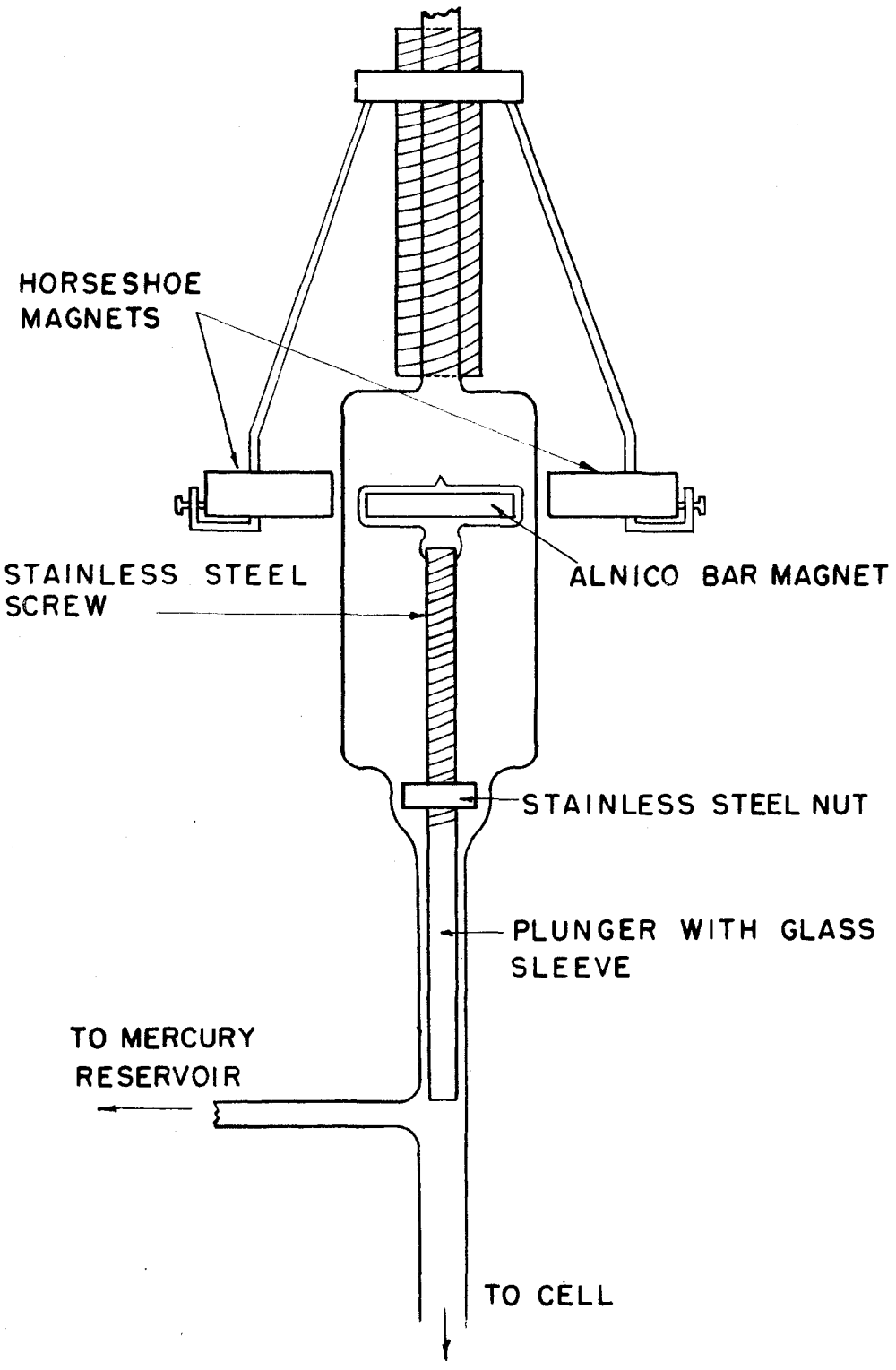

FIGURE 7. DROP CONTROL

plunger was a short distance below the side arm the flow of mercury was stopped. As the plunger was further lowered, mercury was forced from the barrel into a tube connecting the drop control to the drop tip. Thus mercury could be forced to the tip and a drop of desired size formed.

Various methods of operating the plunger were attempted and various materials were used to form the plunger. The first method attempted utilized a ground glass plunger operated by a stainless steel bellows. Both the plunger and the barrel were attached to the bellows through Kovar-glass seals. The bellows was operated by means of a screw. This system worked fairly well, but it was rather fragile, difficult to clean and keep clean, not too easily outgassed, and its use resulted in quite a bit of vibration in the system. Repairs were difficult and time-consuming. It was then decided to try a metal plunger and to operate it with a magnet. Although an electromagnet arrangement was tried, it was discarded because careful control was not possible. Instead, a permanent magnet which was operated manually was used. A bar alnico magnet was attached to the top of the plunger. This magnet was rotated by horseshoe magnets on the outside. As it rotated the threaded upper part of the plunger turned inside a nut, thus raising and lowering the plunger as desired. This system worked very smoothly and permitted excellent control of the drop.

A stainless steel screw-plunger and nut were first used. This worked quite well for a while, but after some time, the "stainless" steel appeared rusted, became stuck frequently, and seemed to

contaminate the mercury--although this may not have been the case. Also, there was some difficulty involved in balancing the nut and securing it into position without breaking the glass. Several other materials such as teflon, nickel, lucite, copper, fiberglass, and carbon were considered. All except copper and carbon were ruled out by consideration of machineability, durability, reaction to heat, or magnetism. The use of copper was questionable both from the standpoint of freedom of motion and from the standpoint of possible reaction with mercury vapor. A carbon screw-plunger and a carbon nut were made. The plunger was covered with a glass sleeve which was ground to fit a glass barrel. The carbon system was self-lubricating and turned freely. However, small particles of carbon apparently worked loose and found their way into the barrel of the drop control. Here, they caused the plunger to "stick" and contaminated the mercury. Nevertheless, this system was used for the first measurements. Two horseshoe magnets were used to operate the plunger.

Since the carbon screw did cause the difficulties mentioned above, it was decided that something else should be tried. Finally a stainless steel screw and nut were again tried, but a glass plunger was attached to the steel screw. Mr. Wayne Jones, with patience and ingenuity, fashioned a drop control of this description which worked beautifully.

4. Cell

The optical properties of the cell have already been described (p. 21). The drop tip was sealed into the cell near one end in order

that it might be focused with the lens used. The drop tip was a 2 mm, i. d., glass tube which was polished until the end appeared straight and flat under a small magnifier. It had to be sealed into the cell parallel to the window and in such a way that the mercury drop would appear approximately in the center of the window. The tip was not completely circular (having a variation in diameter of perhaps 1-2 percent), nor was the inside edge completely free from tiny nicks. It was felt, however, that these small irregularities would not affect the shape of the drop (See Andreas, Hauser & Tucker (3)). The diameter of the drop tip was determined after the tip was sealed into the cell. Thus the diameter measured was the same diameter that was photographed. It was measured on the measuring machine (p. 43) using the "zirconarc" lamp as the illuminating source. This tip diameter was the standard of magnification. It was not so easy to measure the diameter of the photographed tip as it would have been if the tip had been completely flat, but no great difficulty was involved and measurements taken at various points indicated that any error involved was within the limits of the measurements.

5. Other

A tungsten wire was inserted into the tube between the drop control and the cell in order to ground the mercury column since Kemball (23) reported that mercury can pick up an electrical charge during distillation. A series of measurements at one time indicated that there might be a difference in the value of the surface tensions with the column grounded and ungrounded. However, more recent

measurements yielded no difference. The question remained unresolved.

A liquid air trap was placed between the cell area and the nearest stopcock in order to prevent any diffusion of stopcock grease vapor to the mercury.

The part of the system so far described was sufficient for the determination of the surface tension of mercury. In order to study adsorption of vapors, it was necessary to have a vapor inlet system of some sort in addition to the sections already described. This system is described in the following section.

C. Vapor Inlet System

The vapor inlet system must consist of reservoirs for the liquids whose vapors are to be adsorbed, some method of introducing these vapors into the system, and a method of determining the pressures of the vapors. The first vapor inlet system designed and built is shown in Figure 8. G and G' were the liquid reservoirs. These were separated from the rest of the system by a mercury seal on a sintered glass plate. This arrangement held a pressure difference of 5-10 mm of mercury. At low temperatures, which were obtained with liquid air or dry ice traps, no vapor escaped from the reservoirs. H and H' were vapor reservoirs from which the vapor could be forced by raising the mercury level in the reservoirs. These reservoirs also were separated from the system by mercury seals on fine pore sintered glass. K, K', and J were mercury manometers. K and K' measured the pressure in the vapor reservoirs. J measured the pressure of the system and also was used to change the pressure of the vapor

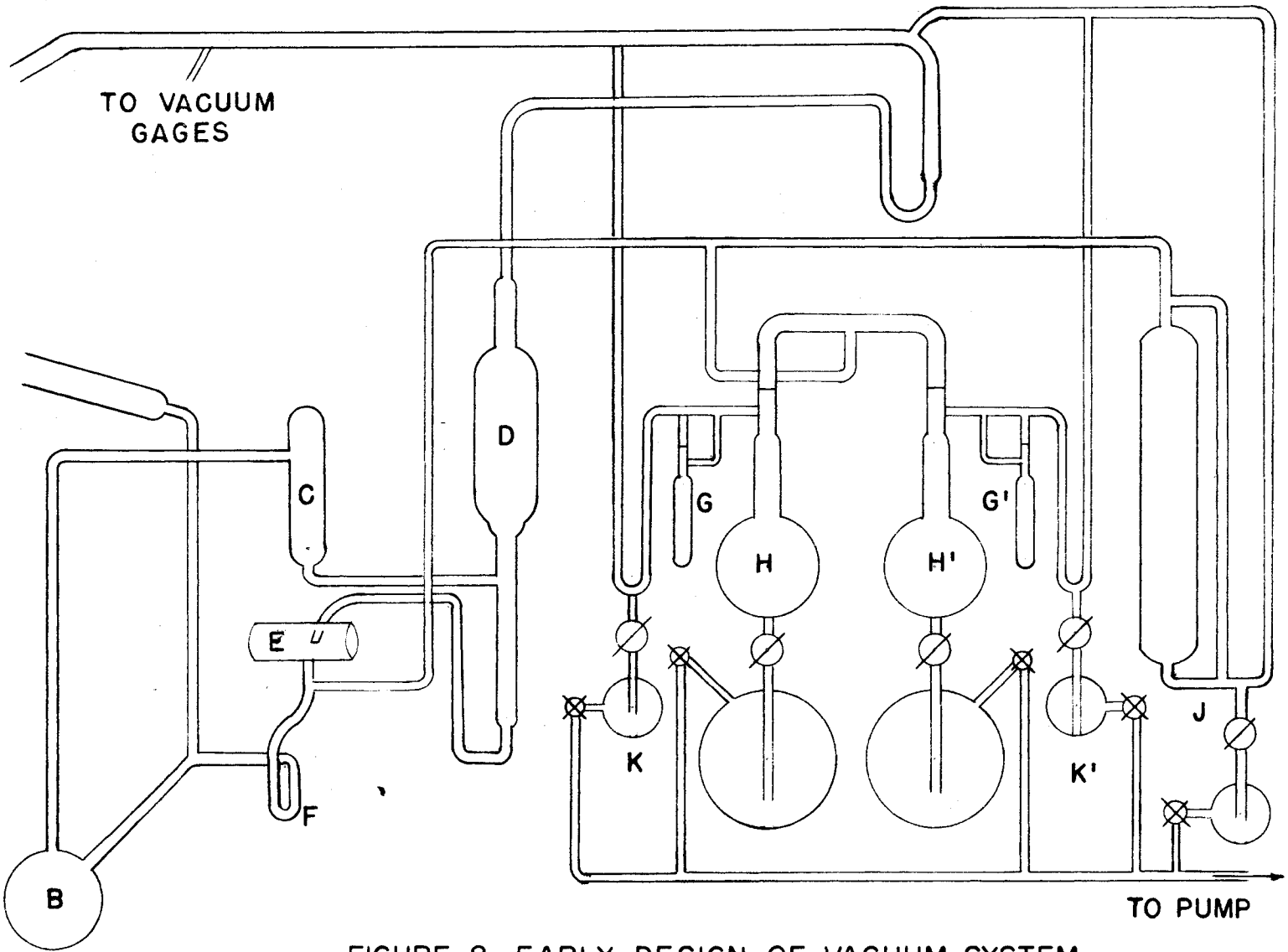

FIGURE 8. EARLY DESIGN OF VACUUM SYSTEM

in the system by raising or lowering the mercury level. Mercury in the U-tube F was frozen with liquid air to prevent vapors from moving beyond the cell.

This design, built to the proper dimensions, was satisfactory although a bit unwieldy. It could have been simplified by eliminating the vapor reservoirs since data obtained by using them was not essential in adsorption studies. This method of introducing vapors was replaced, however, by a simplified system which consisted of liquid reservoirs separated from the system by Fulton valves (Figure 9). A manometer constructed of precision bore 5/8" tubing measured the pressure of the vapor in the system. This method eliminated the mercury reservoirs and also permitted the liquids to be stored in their respective reservoirs without the aid of cold traps to prevent the escape of vapors.

In the final arrangement fine bore porous plates with mercury seals were placed between the valves and the cells. The porous plate-mercury seal arrangement made it easier to control the flow of vapor, indicated when and how fast vapor was flowing, indicated any leaks through the valves, and prevented back diffusion of vapor into the reservoirs.

A sketch of the complete vacuum system is shown in Figure 10. A represents the primary mercury still, B the secondary mercury still, C the mercury reservoir, D the drop control, and E the cell. F represents the U tube in which mercury was frozen when adsorption studies were made. The manometer J was connected to the manifold and the

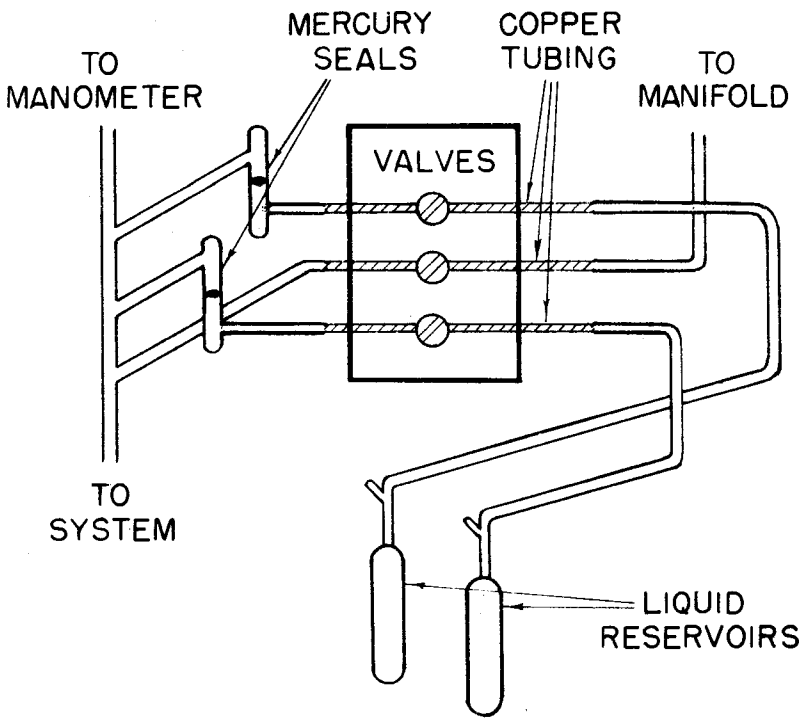

FIGURE 9. VAPOR INLET SYSTEM

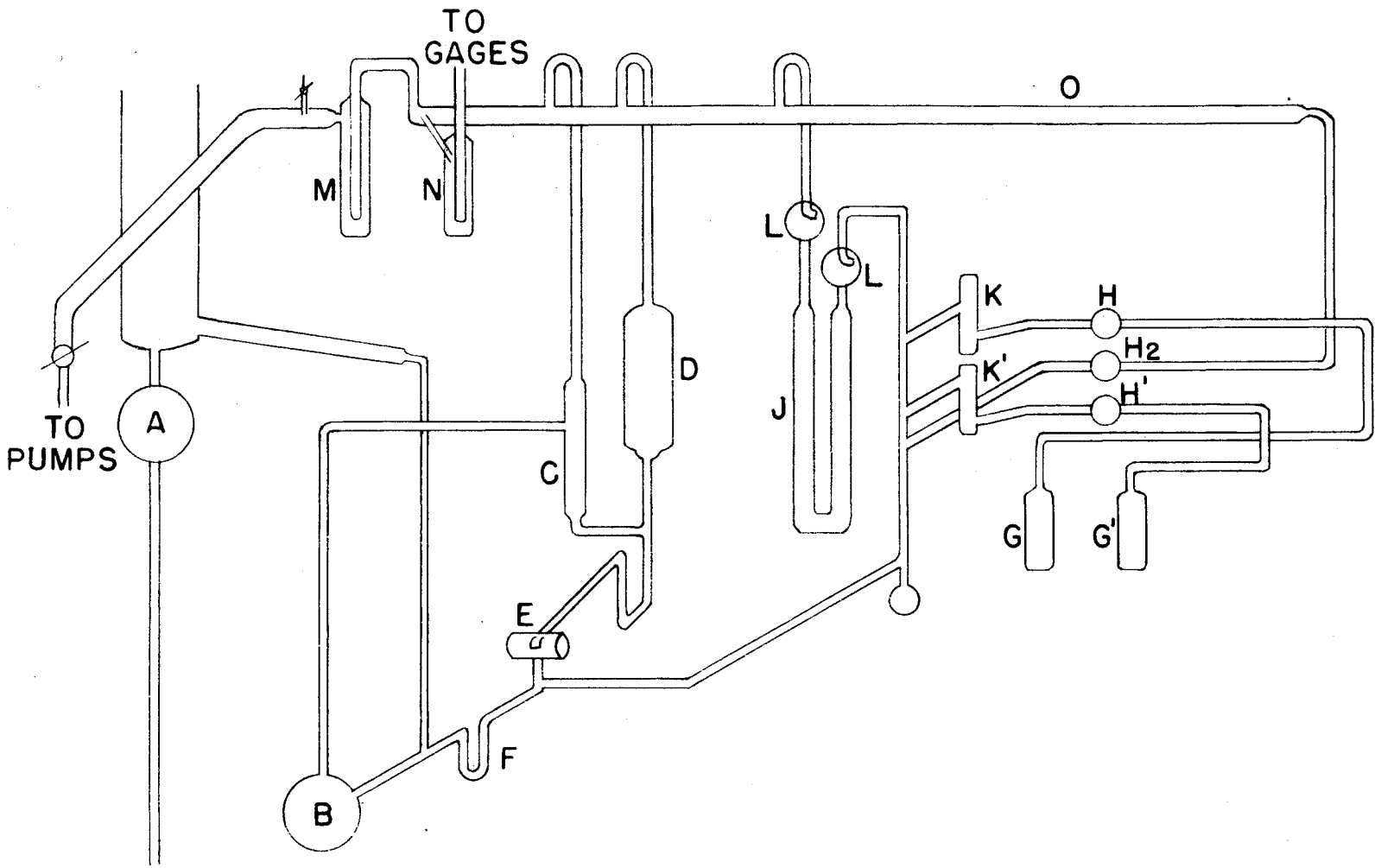

FIGURE 10. PENDENT DROP APPARATUS, VACUUM SYSTEM

system through splash bulbs L. These bulbs were used to prevent loss of mercury when the manometer was outgassed. G and G' represent the liquid reservoirs from which vapor passed through the valves H and H' and the mercury seals K and K' to the system. M represents the trap which separated the area containing stopcocks from the rest of the vacuum system. N represents the trap to which the gages were attached. Liquid air was always used to cool trap N, but dry ice was usually used for trap M. P represents the vacuum manifold. C, D, and J were all attached to the top of the manifold in order to prevent any mercury which may have reached the manifold through outgassing or accident from entering these sections. The connections between E and the valve H2 were designed to prevent mercury from reaching the copper tube connected to the valve. H2 connected the cell area to the vacuum manifold. It was closed during adsorption on measurements and opened to remove vapors or to outgas the system.

D. Vibration Support and Mounting

The system had to be protected from vibration if a sharp image of an equilibrium drop was to be obtained. First attempts to eliminate vibration involved mounting the vacuum rack on rods bolted through the wall and supporting it by bolting the vertical rods to a board separated from the desk top by a layer of sponge rubber. This arrangement proved to be unsatisfactory. Separating the rods from the wall by rubber sleeves and rubber pads helped, but not enough. Even with every source of large vibration, such as fans, hoods, etc., within the

building turned off, fairly satisfactory freedom from vibration could be obtained only between the hours of 1:00 and 3:00 a.m. Since this was inconvenient, a better method of eliminating vibration was sought. It was decided to mount the system on a box-like rack which would be bolted to a soapstone slab. The rack was constructed of an angle iron frame and aluminum cross bars placed at intervals of approximately 6" (Figure 11). It was unusually sturdy. This was mounted on a three inch thick slab of soapstone which rested with one end supported by hard rubber and the other end supported by an inflated inner tube (size 4.00-8). This arrangement dampened vibration remarkably well, particularly if the inner tube was sufficiently inflated. It was also desirable to exclude insects from the work area inasmuch as it was rather annoying to have a moth or other insect fly into the apparatus, thereby imparting violent motion to the mercury drop, just as the photograph was about to be taken.

E. Measuring Machine

A Cambridge Universal Measuring Machine (Cambridge Instrument Company, Ltd., London), which permitted measurement of distances in both the x and y directions with a reproducibility of 0.002 mm was used. The photograph was placed between two glass plates mounted on a carriage. For transverse measurements the table was moved and positions were observed on the transverse scale through a filar microscope. A screw adjustment of the table permitted careful alignment of the object to be measured.

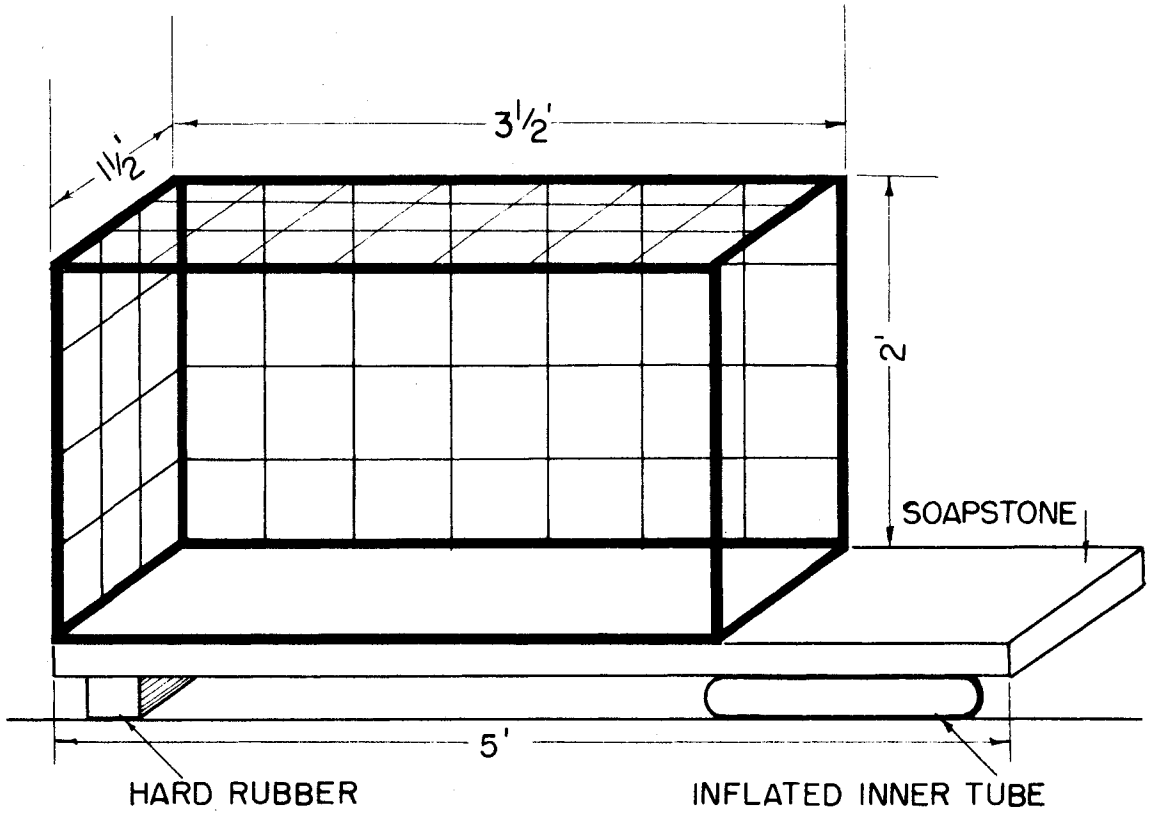

FIGURE 11. VACUUM RACK AND MOUNTING

F. Temperature Control

Since the temperature coefficient of mercury is only about 0.22 dynes per degree, it might be expected that small temperature changes would have little effect upon the surface tension measurements. However, the vapor pressures of both ethanol and heptane change rapidly in the vicinity of 30° C at which temperature these measurements were made. For this reason temperature really should have been controlled within 0.1°, if possible, for best results.

Such a temperature control for this apparatus was not realized. A structure which would completely enclose the apparatus and all parts was begun but not finished. The measurements discussed in this paper were made during a warm part of summer when the temperature varied only a few degrees from 30° C. The apparatus was enclosed on all sides except one by the aforementioned structure. Under these conditions three types of temperature control were used.

1. On some days room temperature remained constant within 0.2° of 30° C.
2. If room temperature was below 30° C two infrared lamps were arranged so that a fan blowing past them blew warm air toward the cell.
3. If room temperature was above 30° C, cooling coils through which cold water was passed were placed so that cooled air was blown toward the cell.

By these methods temperature could be maintained within a 0.2° range over a period of several hours. The temperature was measured

with a 0.1° thermometer placed directly above, and close to, the cell. The temperature was recorded at the time of each photograph.

IV. EXPERIMENTAL

A. Materials

1. Mercury

The first mercury used was simply triply-distilled mercury from the Goldsmith Bros. Smelting and Refining Company. This mercury was distilled into the vacuum system where it was then distilled continuously for several hours. The highest value for the surface tension obtained for this sample of mercury was about 464 dynes/cm. A later sample of mercury was aerated with dry, filtered oxygen for 22 hours before being distilled into the system. The surface tension of this mercury was no higher than was that for the previous sample.

A more careful purification of the mercury seemed in order. A modification of a method of mercury purification described by Bartell and Bard (5) was used. The mercury was caused to fall repeatedly in fine droplets through a column filled with 18 percent nitric acid after which it was washed several times with distilled water and filtered. The filtered mercury was air distilled twice, filtered again, and distilled under vacuum. At this point it was considered ready to be distilled into the system. Values obtained for the surface tension of this mercury sample were still only about 460 dynes/cm.

A somewhat different procedure was followed for the final sample of mercury used. The mercury was first shaken with concentrated nitric acid, then caused to fall through the nitric acid column,

washed, and filtered. It was then stirred with sulfuric acid and air distilled three times being filtered after each distillation. The final step was vacuum distillation after which it was ready to be distilled into the system. The surface tension found for this mercury sample was likewise 460 dynes/cm. The latter two purification procedures were carried out by Lyle Nesbitt of the Physical and Inorganic Group.

2. Heptane

The heptane used in this study was purified by Don Hickson of the Physical and Inorganic Group according to the method of fractional melting described by Aston and Mastrangelo (4). It was reported as at least 99.3 percent pure.

3. Ethanol

The ethanol used had previously been purified by Lyle Nesbitt. The boiling point was given as 78.72°-78.75° C corrected.

B. Procedures

1. Surface tension of mercury

Determination of the surface tension of mercury with this apparatus was relatively simple. Mercury was distilled into the system only after a fairly good vacuum, 10^{-5} mm of mercury or less, had been obtained. Sufficient mercury was distilled into the secondary still to allow for continuous distillation plus a supply of mercury in the drop control and in the mercury reservoir. The mercury was then distilled

continuously for several days or until photographs taken on succeeding days showed no increase in surface tension. When it was desired to photograph a drop of mercury, the plunger of the drop control was lowered enough to stop the inward flow of mercury. Distillation was continued until there was a supply of mercury in the mercury reservoir. The plunger of the drop control was further lowered to form a drop of the proper size on the tip. The photograph was then taken, and the plate developed.

In order to obtain a motionless drop, the secondary still was turned off so that mercury had stopped distilling when the photograph was taken. The forepump, but not the diffusion pump, was also stopped to prevent vibration. Usually about 30 seconds were allowed to elapse between the time the shield of the plate holder was pulled out and the time the picture was taken. This permitted the damping of vibrations caused by putting the plate holder in the camera and pulling out the shield.

In measuring the photographs, the plates were first lined up on the measuring machine by lining up the shadow of the plumb line on the photograph with the cross hairs of the traveling microscope. The maximum diameter was then found and measured after which the second diameter could be found and measured. Since the drop forming tip was not exactly vertical, being perhaps 1°-2° off, it was necessary to realign the plate in order to measure the diameter of the drop-forming tip to determine magnification. The surface tension was calculated from equation (5) taking $g = 980.3$ cm/sec (value at Chicago) and $\rho' = 13.522$ g/cm^3 at 30° C.

2. Adsorption of single vapors

For the determination of adsorption of vapors, additional steps (beyond those described above) included (1) sealing off the cell area from the rest of the system to confine the vapors to this area, (2) allowing vapor to enter the cell area in desired increments, (3) determining the pressure at the time of each measurement, and (4) allowing sufficient time for equilibrium to be established before taking the photograph. In all cases the liquids had been outgassed by alternate freezing and melting until no bubbles were observed upon melting. This required 4-6 freezings usually. Vapors were confined to the cell area by freezing the mercury in the U-tube between the cell and the secondary still (F in Figure 8). It was necessary that mercury extend for some distance above the U-tube to prevent condensation of vapors on the cold mercury surface. The methods of introducing vapor to the system and of determining pressure were different for the original and final systems used. Both of these will be discussed.

a. Original method. The original system is that shown in Figure 8. The following procedure was developed using this system. Mercury was raised in the manometer of the liquid concerned (G or G'). Mercury was raised only a short distance in J. The cold trap was then removed from the liquid reservoir, and vapor was allowed to bubble in until the pressure in the system (as determined by J) was at the lowest value to be measured. The system was given a chance to come

to equilibrium, the photograph was taken, and the pressure was read from the manometer and recorded. The mercury in the manometer *J* was then raised enough to change the pressure the desired amount and the process was repeated. After the mercury had been raised to the top of the manometer, it could be lowered again, additional vapor admitted until the pressure of the vapor in the system was just above the highest pressure obtained before. The complete process described above could then be repeated.

b. Final method. The data reported here were obtained with the apparatus as shown in Figure 10. The cell area was isolated from the rest of the system by freezing mercury in the U-tube as described before (the mercury was frozen either with liquid nitrogen or dry ice and acetone and was kept frozen over a period of time with dry ice and acetone) and by closing the valve (H2) to the manifold. The vapor in question was then introduced by opening the proper valve slightly and letting vapor bubble through the mercury seal until the desired pressure was reached. The pressure was read immediately after the photograph had been taken. A cathetometer was used to read the pressure to 0.1 mm. Temperature was also recorded after each photograph. In order to obtain the higher pressures it was necessary to warm the liquid in the reservoirs slightly (heat from the hand was sufficient). The vapor could be pumped out in preparation for measuring the effect of the other vapor by opening the valve to the vacuum manifold.

3. Adsorption of mixed vapors

Mixed vapor adsorption measurements were carried out as single vapor measurements were except that two vapors were now admitted and the pressure of each was desired.

a. Original method. Mercury was raised in both manometers G and G'. The mercury level in the vapor reservoirs H and H' was adjusted to the top of the capillary tubing. Vapor from one of the liquid reservoirs was allowed to bubble into the vapor reservoir, but not enough to bubble out of this reservoir. The pressure of this vapor was recorded. The mercury in the vapor reservoir was then raised to the 300 ml mark. After vapor had stopped bubbling out, the pressure was recorded. The mercury was again lowered to the top of the capillary and the pressure of the remaining vapor read and recorded. The pressure of the system as measured on manometer J was recorded. This process was repeated with the two vapors until the desired mixture was obtained. Assuming Dalton's law of partial pressures, the pressure of one of the vapors could be read from the manometer J and the pressure of the second determined from the difference between this value and the final total pressure. If this apparatus had been simplified by the removal of the vapor reservoirs as indicated on page 39 , the vapor could have been bubbled directly into the system from the liquid reservoirs, adding first one vapor, then the other, until the desired pressures were reached.

In order to pump off vapors before making a second series of

measurements, the mercury in the U-tube was allowed to melt. The vapors were then pumped out through this tube until the pressure was low enough that the mercury could be lowered out of J.

b. Final method. The values for mixed adsorption of ethanol and heptane here presented were obtained in the following manner. After the cell area had been isolated as previously described, ethanol vapor was introduced until the desired pressure was reached. This pressure was read and recorded. Heptane was then admitted in desired increments. Photographs were taken after one hour had elapsed. One hour was rather arbitrarily chosen as the time to permit equilibrium to be reached. A couple of series of photographs did indicate that this was more than an adequate amount of time. Pressure and temperature were recorded immediately after each photograph. When one series of photographs had been taken, the vapors were pumped out. Ethanol was then admitted until another desired pressure was obtained and a new series of measurements was made. Usually one mercury drop was used for each series of measurements.

C. Results

Values obtained for the surface tension of mercury have already been indicated. Measurements were made over a period of about two years. During this time three different dropping tips and three different drop controls were used. Mercury samples which had undergone four different types of treatment were measured. In all cases the surface tension obtained was within 1 percent of 460 dynes/cm.

The mercury column was grounded by means of a tungsten wire sealed through the glass. Values obtained with the grounded and ungrounded mercury were not noticeably different during the most recent studies. However, results on this were not conclusive.

Particularly before the apparatus was assembled the last time all the glass was carefully cleaned with nitric acid or cleaning solution or both. It was then rinsed with distilled water. The system was also outgassed before mercury was distilled in. The cold trap N in front of the last stopcock was kept filled to prevent diffusion of any vapor from stopcock grease. The average of four photographs taken before and during the studies with adsorption of the vapors gave a value of 461 dynes/cm. This latter value was used in determining surface tension lowering.

The values obtained for surface tension lowering for the single vapors are shown in Tables 1 and 2 and graphically in Figures 12 and 13. Values obtained for the same vapors a year earlier using the first method described (page 50) are in fairly good agreement with these latter ones. The heptane data agree well with those of Kemball and Rideal (24). The curve for ethanol falls considerably below that obtained by Kemball (26).

The values obtained for mixed adsorption are given in Table 3 and are shown graphically in Figures 12 and 13.

Table 1. Surface Tension Lowering of Mercury by n-Heptane at 30° C

Surface tension mercury = 461 dynes/cm

p(mm Hg)	π(dynes/cm)
1.0	30
4.2	36
13.1	46
16.6	46
17.7	49
27.5	54
32.7	56
40.2	61
47.4	63
52.5	65

Table 2. Surface Tension Lowering of Mercury by Ethanol at 30° C

Surface tension mercury = 461 dynes/cm

p(mm Hg)	π(dynes/cm)
1.7	9
2.2	11
6.7	22
9.4	26
16.9	33
21.8	43
25.9	43
35.1	47
45.0	49
51.5	54
58.9	53
60.8	56
70.2	62

Table 3. Surface Tension Lowering of Mercury by n-Heptane-Ethanol Mixtures at 30° C

Surface tension mercury = 461 dynes/cm

p_E = 11.5 mm		p_E = 27.5 mm	
p_H(mmHg)	π (dynes/cm)	p_H(mmHg)	π (dynes/cm)
4.1	44	4.4	48
9.2	45	14.6	53
16.8	50	25.5	56
29.3	57	41.7	61
34.5	59	51.6	66
44.6	65		
57.4	69		

p_E = 41.2 mm	
p_H(mmHg)	π (dynes/cm)
4.1	54
10.2	59
19.4	63
25.5	63
40.1	65

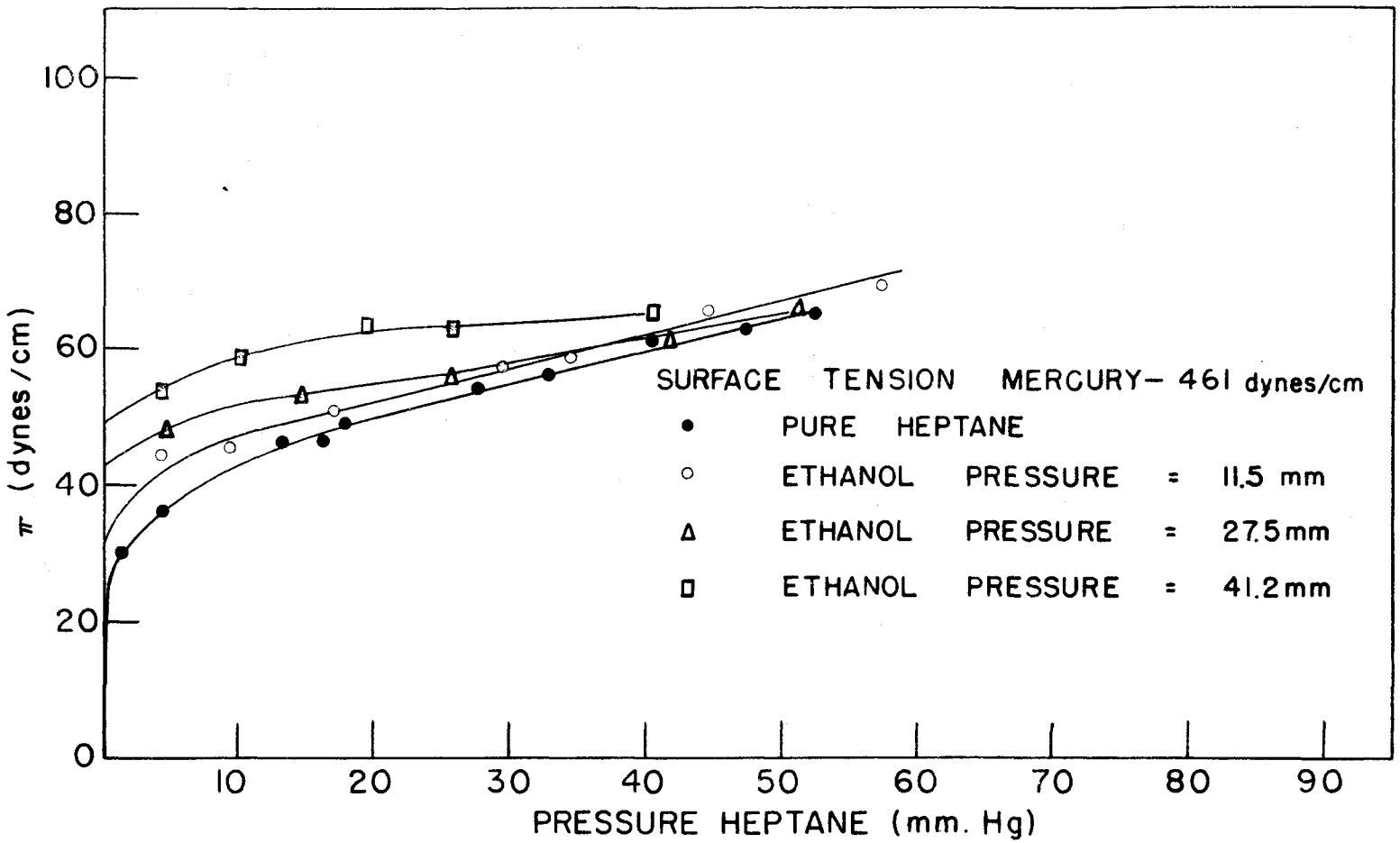

FIGURE 12. SURFACE TENSION LOWERING OF n-HEPTANE AND HEPTANE-ETHANOL MIXTURES AT 30°C

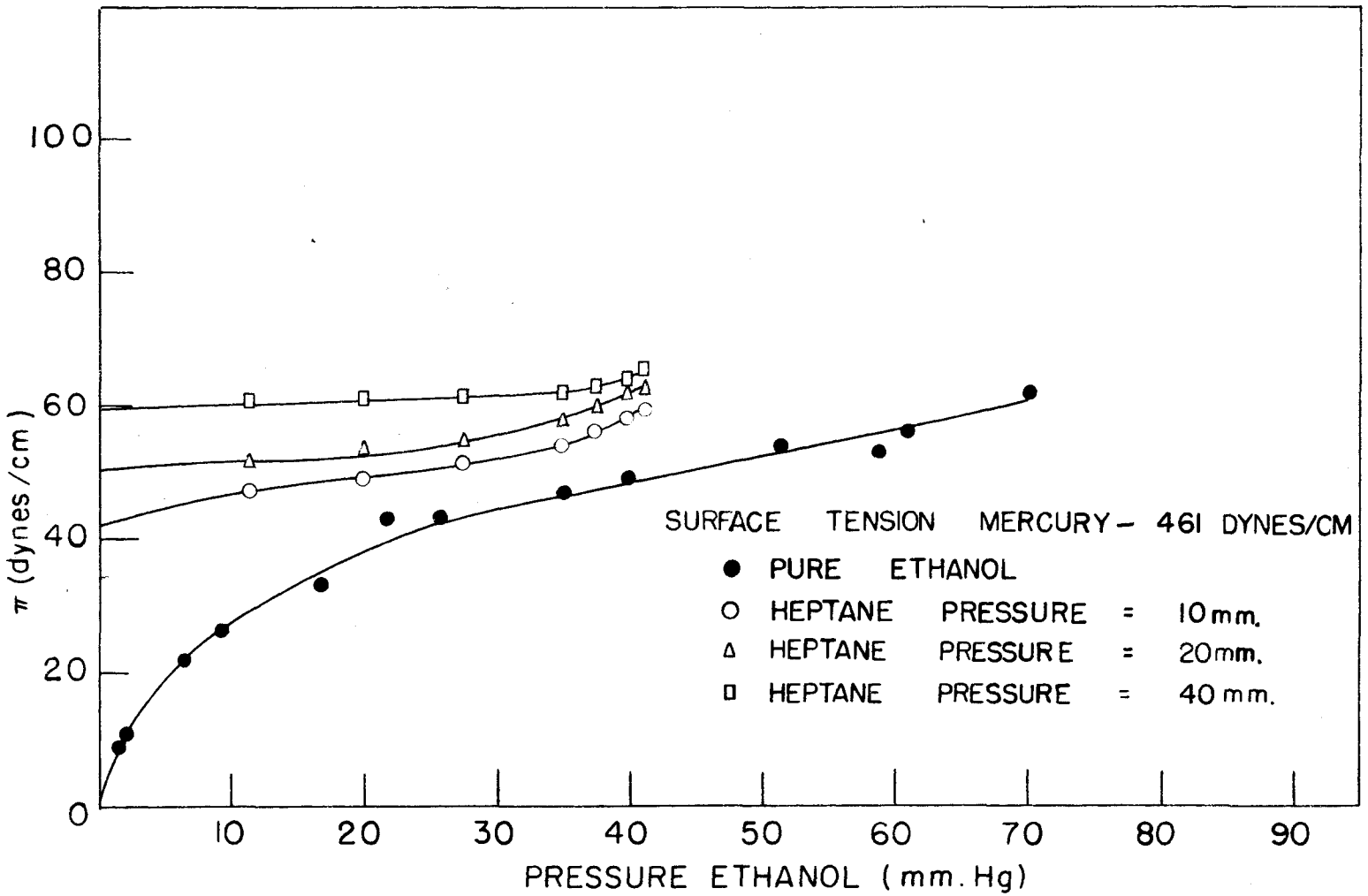

FIGURE 13. SURFACE TENSION LOWERING OF ETHANOL AND ETHANOL- n-HEPTANE MIXTURES (CROSS PLOT) AT 30°C

V. DISCUSSION

A. Apparatus

The design of a pendent drop apparatus for the study of surface tension of mercury in vacuum was fraught with several problems. It is felt that most of these were satisfactorily solved. The focal point of the apparatus was the cell which housed the drop-forming tip. The cell used was an absorption cell with optically flat windows of specifications already given. The drop-forming tip was made from a piece of small bore tubing which was cut and ground to a flat surface. A few small nicks did remain on the inside surface (since mercury does not wet glass, this is the important surface) and the tip was probably not completely circular. However, it is felt that these small imperfections did not affect the shape of the drop (see Andreas, Hauser, and Tucker (3)). The tip was measured after it was sealed in the tube so that the side measured was the one which was later photographed to serve as magnification standard.

Devising a method of controlling the drop size within a vacuum system was one of the most difficult problems. In connection with this the flow of mercury to the drop control apparatus had to be controlled. In addition this had to be accomplished without the use of any stopcocks which would involve the use of stopcock grease. These problems were solved simultaneously with the drop control system previously described. This consisted of a magnetically operated plunger

which controlled both the flow of mercury and the size of the drop. Considerable difficulty was involved in the construction of this drop control because the tolerances were small and alignment was critical. After it was properly constructed, however, it worked very smoothly and was quite satisfactory.

Stopcocks were used on either side of the diffusion pump and a stopcock air inlet was attached to the vacuum manifold. A trap was placed between this last stopcock and the system so that so long as liquid nitrogen or dry ice surrounded this trap no stopcock grease should have been able to reach the system.

The introduction of vapor to the system was accomplished with the use of metal valves in connection with mercury seals on porous plates. Some difficulty was experienced in obtaining valves that did not leak. The valves on this apparatus were not used for a very long period of time, but they worked quite well during the course of these measurements.

A vacuum of 10^{-5} mm of mercury could be readily obtained in this system. After the pumps had been operating for a few hours the pressure fell to 4 or 5 X 10^{-6} mm. These pressures are, of course, exclusive of mercury vapor or any other vapor that would be condensed out by liquid nitrogen.

Temperature control should be improved so that temperature can be held constant to 0.1° or better, if possible. Throughout the mixed adsorption measurements the temperature was $30^{\circ} \pm 0.2^{\circ}$. During the course of single vapor measurements, the temperature varied as much as 0.5°. Any error due to this much temperature variation, however, was

probably within experimental error. If the apparatus were completely enclosed and an adequate blower used, it should be possible to control the temperature automatically within desired limits. (The temperature control method used in this work was arranged manually and changed as necessary to maintain the temperature desired.) The use of a constant temperature jacket around the cell was considered, but no satisfactory arrangement was found. This method was complicated by the necessity for keeping the cell windows free and by the tubes attached to the cell.

B. Optical System

The optical system used in this work was not entirely satisfactory. Apparently not much is known about the theory of profile projection. At any rate, it was difficult to find information on the subject. The concentrated arc light source is the nearest thing to a point source that has been developed and should be the best type of light source for this work. The housing of the lamp used in this work could be moved in various directions. It was important then that the proper position be found and the housing firmly fastened in this position. The lens, while not perfect, seemed to be satisfactory (see page 20). The measurements with calibrated steel balls (page 27) indicated that its performance was adequate. The camera, on the other hand, was not completely satisfactory and should be built more rigidly with special attention being paid to see that both the back and front plates are exactly and rigidly perpendicular to the optical axis. This should not be too difficult to accomplish. The

mercury drop was magnified about 15 times on the photographic plate. This seems to be a workable magnification, and so it would seem desirable to build a camera that could give this much magnification.

The photographic plates adopted were completely satisfactory as was the measuring machine.

Possible sources of error due to the optical system have already been discussed (page 24). It was felt that if the component parts of the optical system were properly aligned and the image was properly focused, the uncertainty of the surface tension would have been within one dyne/cm or 0.25 percent. Unfortunately the above requirements were not met for all the photographs used in this study. For this reason, calculations were made using measurements to only 0.01 mm. The uncertainty was therefore somewhat more than 1 dyne/cm, and in some cases it was near 2 dynes/cm due to improper alignment and improper focusing which led to uncertainty as to where measurements should be made. Values here given are thus to be taken as $\pm$ 2 dynes/cm. The pressures are probably accurate within 0.2 mm.

C. Results

In attempting to explain the value obtained for the surface tension of mercury, it is necessary to consider the consistency of the results under different circumstances and the results of adsorption of single vapors as compared with those obtained by Kemball whose value for the surface tension of mercury was 23 dynes/cm or about 5 percent higher than that obtained in this work. The adsorption of heptane obtained on this mercury was in agreement with that obtained by Kemball while

the adsorption of ethanol obtained was considerably less than that obtained by Kemball. One explanation of these results would be that the mercury, all of which came from the same source, contained a difficult-to-remove impurity which lowered the surface tension by approximately 23 dynes/cm. The adsorption of heptane then seemed to be independent of the presence of this impurity while the ethanol adsorption was hindered by its presence.

It might be interesting to measure the surface tension of mercury prepared by a different company. Also an even more careful purification procedure might be tried. No change in the surface tension of mercury samples used was noted after continuous distillation for a period of three or four days, but distillation for a longer period of time might be tried.

In order to interpret the adsorption data, it was deemed desirable to find a theoretical equation which would give results in agreement with the experimental results. Since the vapors adsorbed in this work were adsorbed on a liquid surface which was presumed to be homogeneous, it seemed reasonable to assume a mobile monolayer obeying a gaseous film equation of state. If a satisfactory expression for the adsorption of single components could be found, it was felt that this could possibly be extended to the case of two components adsorbed on the same adsorbent.

The adsorption of both ethanol and heptane has been studied by Kemball and Rideal as indicated previously. In order to explain their results these workers applied the Volmer equation for gaseous films

$$\pi (A-a) = KT \quad \text{where} \tag{7}$$

π = lowering of surface tension,

A = area per molecule,

a = co-areas of molecules, and

K and T have their usual significance

and felt that their data were satisfactorily interpreted with the aid of this equation. Accordingly the first attempt to explain the data obtained in the present work was an application of the Volmer equation. The equation as written above was combined with the Gibbs adsorption equation $\Gamma = \frac{1}{KT} \frac{d\pi}{d\ln p}$ where Γ = molecules adsorbed per cm^2 and the relationship $A = \frac{1}{\Gamma}$

to give an equation of the form $\ln \frac{\pi}{KT} = \ln p - \frac{a\pi}{KT} + c$ (8)

or $\pi = Cpe^{-\frac{a\pi}{KT}}$ where a, c, and C are constants. (9)

Constants for this expression were evaluated in the more convenient form $\pi = C_1 p_{10}^{-a_1\pi}$. The best values for heptane gave

$$\pi = 119\ p_H 10^{-0.033\pi} \tag{10}$$

while the best values for ethanol gave

$$\pi = 6.92\ p_E 10^{-0.0154\pi} \tag{11}$$

where p_H represents the pressure of heptane and p_E represents the pressure of ethanol.

Comparisons of calculated and experimental values for π vs. p are shown in Figures 14 and 15. It can be seen that agreement is good except for the high pressure range of heptane.

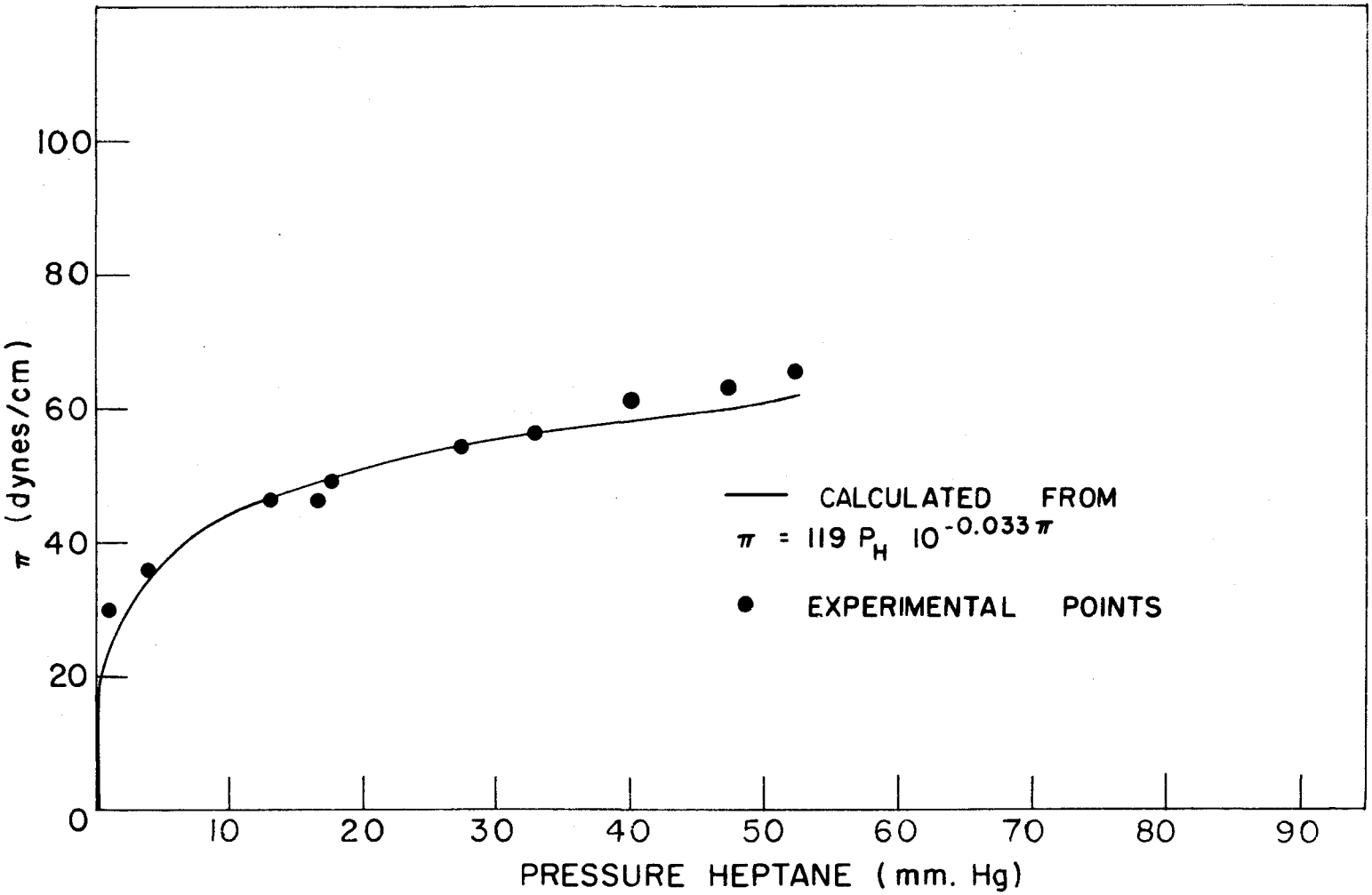

FIGURE 14. CALCULATIONS FROM AN EQUATION OF THE TYPE $\pi = CPe^{-a\pi}$ COMPARED WITH EXPERIMENTAL VALUES FOR n-HEPTANE

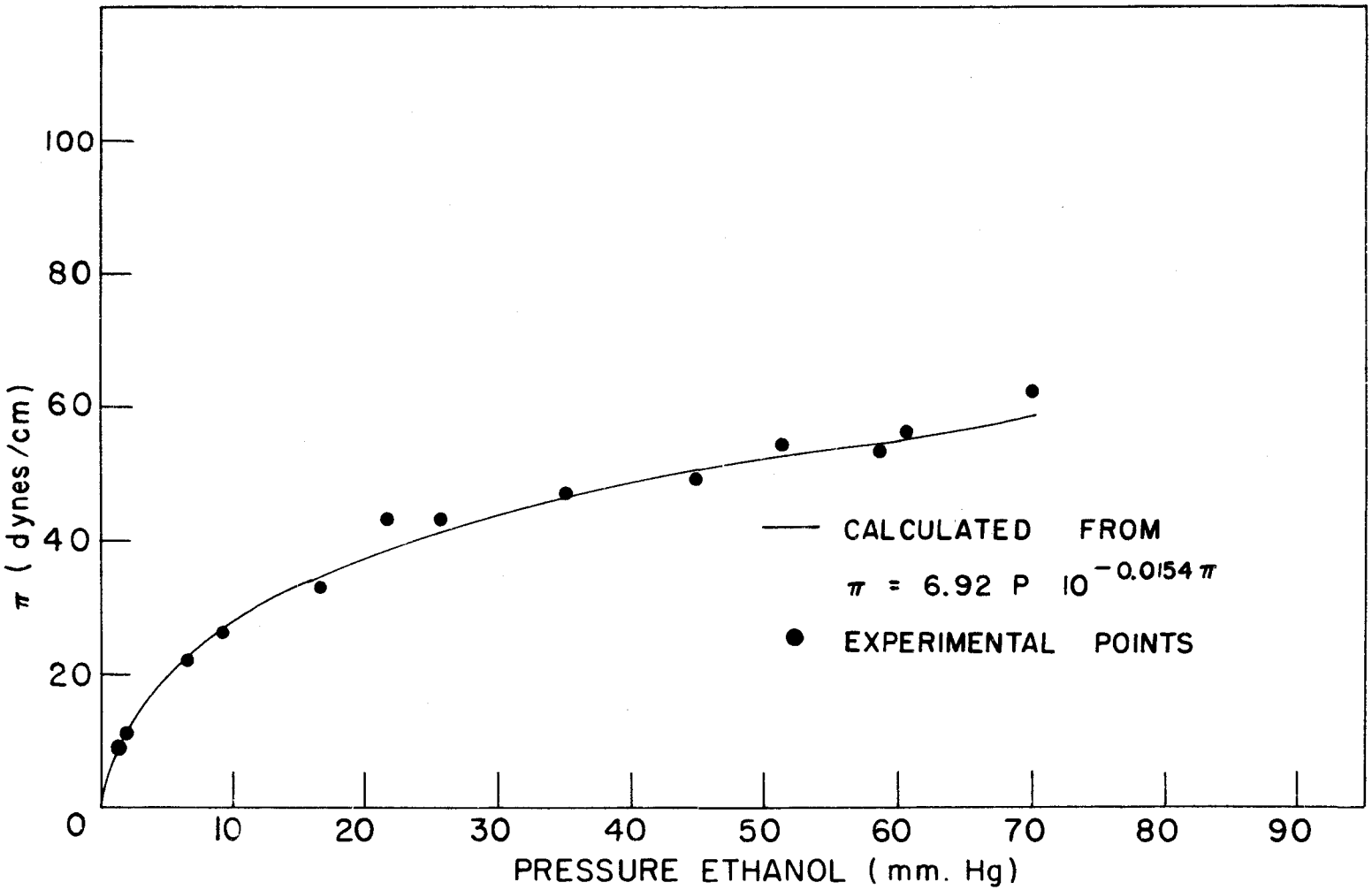

FIGURE 15. CALCULATIONS FROM AN EQUATION OF THE TYPE $\pi = CPe^{-a\pi}$ COMPARED WITH EXPERIMENTAL VALUES FOR ETHANOL

In order to apply the treatment to two components, the expressions

$$(A - \frac{a_1\Gamma_1 + a_2\Gamma_2}{\Gamma_1 + \Gamma_2}) = KT$$

$$\frac{d\pi}{KT} = \Gamma_1 d\ln p_1 + \Gamma_2 d\ln p_2$$

$$A = \frac{1}{\Gamma_1 + \Gamma_2}$$ (The subscripts refer to each of two components.)

were combined to give

$$\pi = c_1 p_1 e^{\frac{-a_1\pi}{KT}} + c_2 p_2 e^{\frac{-a_2\pi}{KT}} \qquad (12)$$

where single component isotherms are special cases. Values calculated from this equation are compared with experimental values in Figure 16. The agreement is not too bad, but one might wish to do better.

A simple interpretation of the Volmer equation would lead one to believe that a correction for deviation from ideal behavior is made for the area of the molecules only. It might well be expected that an interaction existed between the molecules, especially at the higher pressures, and that the introduction of a term accounting for this interaction would lead to an equation more in accord with the results. Such a term was introduced by writing

$$\pi = cpe^{-\alpha\pi + \beta\pi^2}$$, where α and β are constants, (13)

for single components and

$$\pi = c_1 p_1 e^{-\alpha_1\pi + \beta_1\pi^2} + c_2 p_2 e^{-\alpha_2\pi + \beta_2\pi^2} \qquad (14)$$

for two components.

The constants for these expressions were determined by rewriting

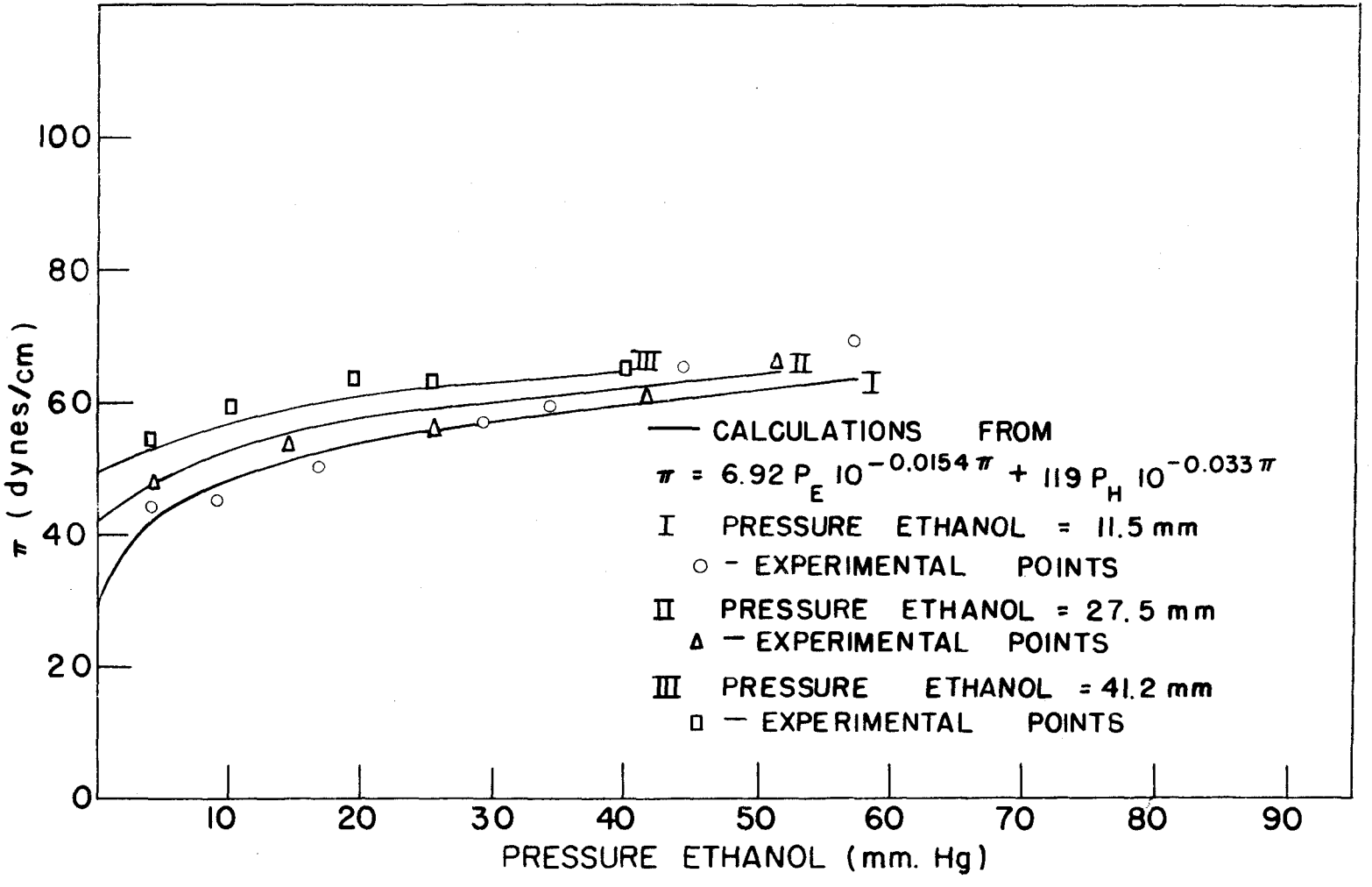

FIGURE 16. CALCULATIONS FROM AN EQUATION OF THE FORM $\pi = C_1P_1e^{-a_1\pi_1} + C_2P_2e^{-a_2\pi}$ COMPARED WITH EXPERIMENTAL VALUES FOR n-HEPTANE - ETHANOL MIXTURES

the equation for a single component in the form

$$\log \frac{\pi}{p} = \log c - a\pi + b\pi^2 . \qquad (15)$$

Log $\frac{\pi}{p}$ was plotted against π and the slopes at several points were determined. These slopes were then plotted against π and the best straight line was drawn through the points. The slope of this line was 2b and the intercept was -a. Log $\frac{\pi}{p}$ could then be plotted against $(-a\pi + b\pi^2)$. The intercept of the straight line obtained from this plot was a constant corresponding to log c. (Equation 15 is of the form $y=c-ax+bx^2$. Hence $y' = -a + 2bx$. After the constants a and b have been determined, the equation can be written in the form y = c + z in order to determine the final constant.) Best values obtained for heptane gave

$$\log \frac{\pi}{p} = 3.42 - 0.091\pi + 0.00615\pi^2 \qquad (16)$$

while best values obtained for ethanol gave

$$\log \frac{\pi}{p} = 1.12 - 0.030\pi + 0.00018\pi^2 \qquad (17)$$

The equations could be written in the original form as

$$\pi = 2630\ p_H e^{-0.210\pi + 0.00142\pi^2} \qquad (18)$$

$$\pi = 13.2\ p_E e^{-0.069\pi + 0.00041\pi^2} \qquad (19)$$

Comparisons of values calculated from these equations are shown in Figures 17 and 18. Agreement in both cases is seen to be good. Values obtained for the two-component systems are shown in Figure 19. Agreement with experimental data is fairly good for the system of lowest ethanol pressure, is not bad for the system of highest ethanol

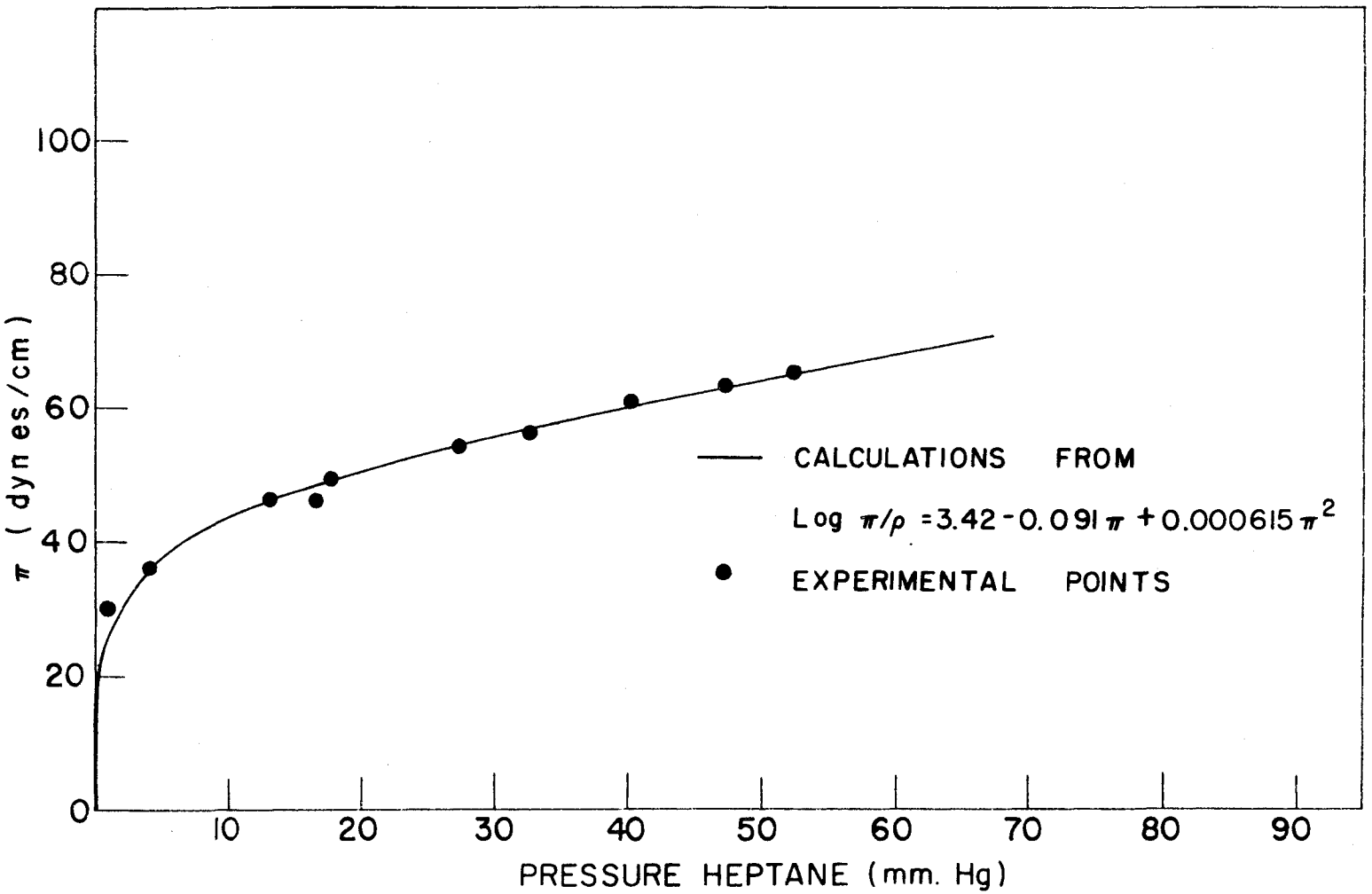

FIGURE 17. CALCULATIONS FROM AN EQUATION OF THE FORM $\pi = CPe^{-a\pi+\beta\pi^2}$ COMPARED WITH EXPERIMENTAL VALUES FOR n-HEPTANE

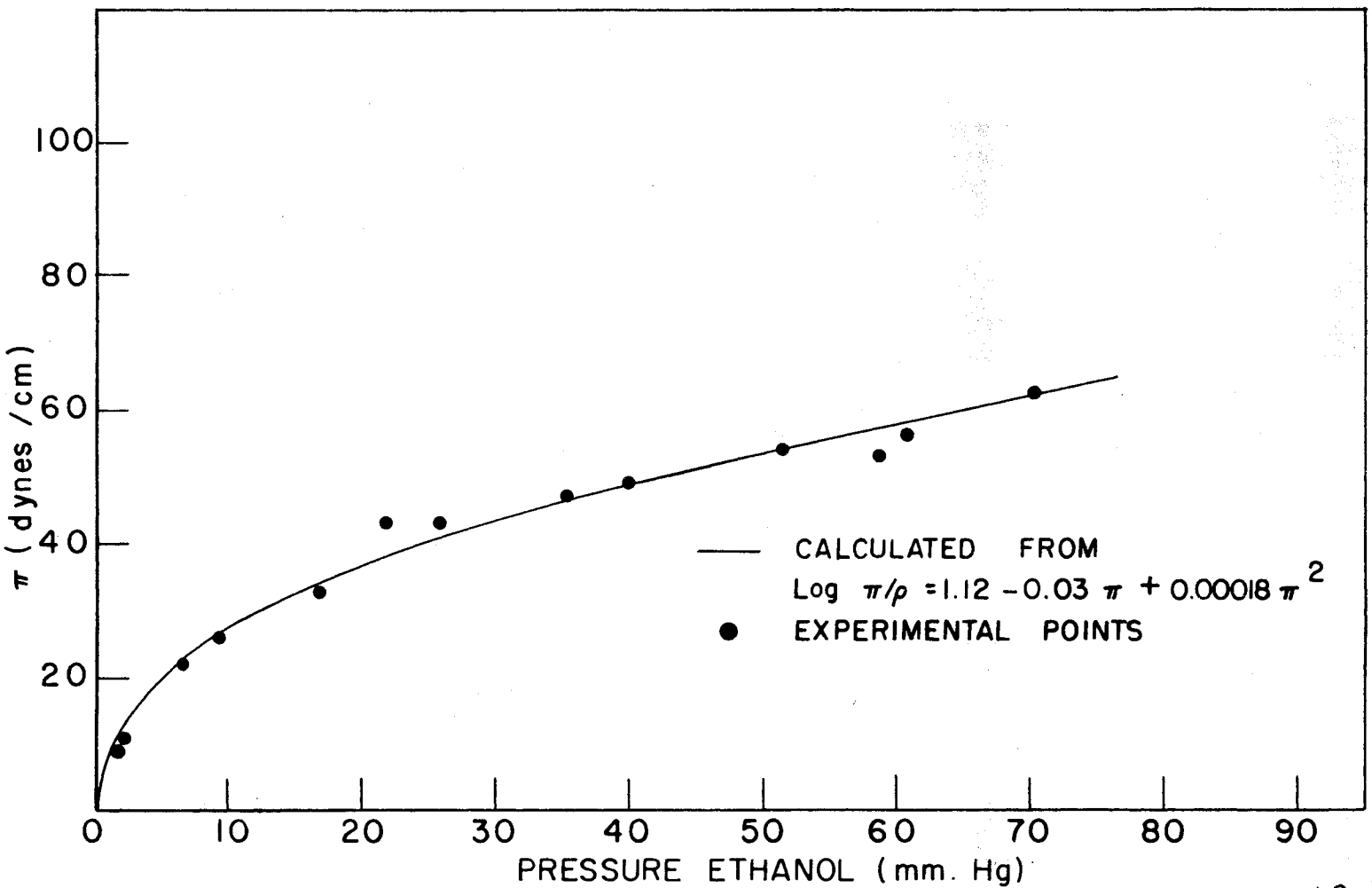

FIGURE 18. CALCULATIONS FROM AN EQUATIONS OF THE FORM $\Pi = CPe^{-a\pi+\beta\pi^2}$ COMPARED WITH EXPERIMENTAL VALUES FOR ETHANOL

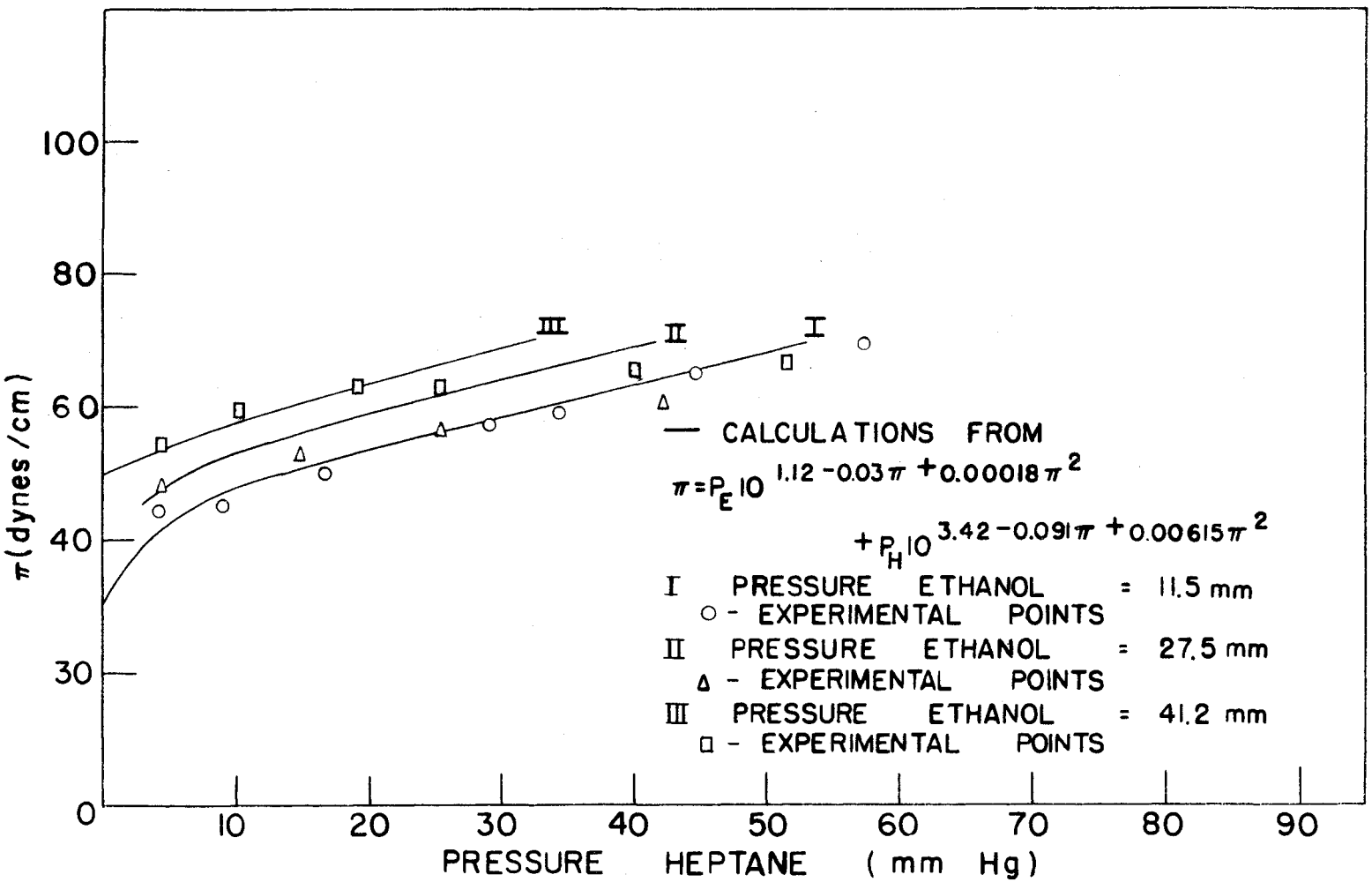

FIGURE 19. CALCULATION FROM AN EQUATION OF THE FORM $\pi = C_1 P_1 e^{-a_1\pi_1} + B_1\pi^2 + C_2 P_2 e^{-a_2\pi} + \beta_2\pi^2$ COMPARED WITH EXPERIMENTAL VALUES FOR n-HEPTANE-ETHANOL MIXTURES

pressure at low heptane pressure, but fails to account for any part of the intermediate system.

Adsorbed gaseous films are generally treated as two-dimensional analogues of three dimensional gases. Hence surface analogues of equations for perfect and imperfect gases can be derived. The general equation of state known as the virial equation of state may be expressed in its simpler forms as $pv = A + \frac{B}{v} + \frac{C}{v^2} + ...$

or $pv = A + Bp + Cp^2 + ...$, where A, B, and C are constants.

A statistical derivation of the virial equation for 3 dimensional gases is given by Fowler and Guggenheim (19) and also by Mayer and Mayer (29). These results may be extended to the two dimensional case giving an equation of the form

$$\frac{\pi A}{KT} = 1 + B\pi + C\pi^2 + ... \qquad (20)$$

The surface analogue of the van der Waals equation

$$\left(\pi + \frac{a}{A^2} \right) (A - b) = KT \qquad (21)$$

may be rewritten in the virial form as

$$\frac{\pi \overline{A}}{KT} = 1 + \pi \left(\frac{b}{KT} - \frac{a}{K^2T^2}\right) + \pi^2 \left(\frac{2ab}{K^2T^2} - \frac{a^2}{K^3T^3}\right) \qquad (22)$$

If equation 22 is compared with equation 20 it can be seen that the second and third virial coefficients can be equated to $\left(\frac{b}{KT} - \frac{a}{K^2T^2}\right)$ and $\left(\frac{2ab}{K^2T^2} - \frac{a^2}{K^3T^3}\right)$ respectively. If only the first two terms

are considered, the expression can be rewritten as $(A - \alpha) = KT$ where $\alpha = b - \frac{a}{KT}$. This equation is formally equivalent to the Volmer equation. Now, if the van der Waals constant a is assumed to depend upon interaction of the molecules and the constant b to be a function of the area of the molecules, the constant of the Volmer type equation contains an interaction term as well as an area correction term. In that case the use of this constant to calculate molecular co-areas is open to some question.

In order to determine the equation of state implied by equations 13 and 14 the expressions for single components

$$\pi = cpe^{-\alpha\pi + \beta\pi^2}$$

$$\Gamma = \frac{1}{A}$$

$$d\pi = KT\,\Gamma\, d\ln p$$

were written. Hence $\frac{d\pi}{d\ln p} = KT\Gamma$ and $\frac{d\pi}{dp} = ce^{-\alpha\pi + \beta\pi^2} - (\alpha\frac{d\pi}{dp} - 2\beta\pi\frac{d\pi}{dp})\, cpe^{-\alpha\pi + \beta\pi^2}$.

The latter equation was rearranged to give

$$\frac{d\pi}{dp} = \frac{ce^z}{1 + (\alpha - 2\beta\pi)\, cpe^z}$$

where $z = (-\alpha\pi + \beta\pi^2)$ whence

$$p\frac{d\pi}{dp} = \frac{cpe^z}{1 + (\alpha - 2\beta\pi)cpe^z}z = KT\Gamma = \frac{KT}{A}.$$

This latter expression in turn can be rearranged to give

$$1 + (\alpha - 2\beta\pi)\pi = \frac{A}{A - (\alpha - 2\beta\pi)\, KT}$$

whence $\pi A = KT + (\alpha - 2\beta\pi)\, KT\pi$

or $$\frac{\pi A}{KT} = 1 + \alpha\pi - 2\beta\pi^2 \qquad (23)$$

from which it is seen that the constants α and β are related to the second and third virial coefficients. A comparison of this equation with equation 22 shows that α can be set equal to $\left(\frac{b}{KT} - \frac{a}{K^2T^2}\right)$ and β can be set equal to $\frac{1}{2}\left(\frac{2ab}{K^2T^2} - \frac{a^2}{K^3T^3}\right)$ in terms of the van der Waals constants.

For two components the expressions

$$\pi = c_1 p_1 e^{-\alpha_1\pi} + \beta_1\pi^2 + c_2 p_2 e^{-\alpha_2\pi} + \beta_2\pi^2$$

$$d\pi = \Gamma_1 KT\, d\ln p_1 + \Gamma_2\, d\ln p_2$$

were written. These equations can be combined in a manner analogous to that given above to give

$$\Gamma_1 + \Gamma_2 = \frac{\pi}{KT}\left[1 - (\alpha_1 - 2\beta_1\pi)KT\Gamma_1 - (\alpha_2 - 2\beta_2\pi)KT\Gamma_2\right].$$

Substitution of

$$\frac{\Gamma_1}{\Gamma_1 + \Gamma_2} = x_1 \; ; \quad \frac{\Gamma_2}{\Gamma_1 + \Gamma_2} = x_2 \; ; \text{ and } \quad \frac{1}{\Gamma_1 + \Gamma_2} = A$$

gives

$$1 = \frac{\pi A}{KT}\left[1 - \frac{(\alpha_1 - 2\beta_1\pi)KTx_1 + (\alpha_2 - 2\beta_2\pi)KTx_2}{A}\right]$$

which can be rewritten in the form

$$\frac{\pi A}{KT} = 1 + (\alpha_1 x_1 + \alpha_2 x_2)\pi - 2(\beta_1 x_1 + \beta_2 x_2)\pi^2 \qquad (24)$$

Equations 13 and 14 thus correspond to an equation of state involving the first three terms of the virial equation in which the second and third virial coefficients are arithmetic means of the constants for the single components. The van der Waals constants for a mixture are often taken as

$$a_m = a_1 x_1^2 + 2a_{12} x_1 x_2 + a_2 x_2^2$$

$$b_m = b_1 x_1^2 + 2b_{12} x_1 x_2 + b_2 x_2^2$$

where $a_{12} = \sqrt{a_1 a_2}$, $b_{12} = (b_1 + b_2)/2$ and the subscript m denotes mixture (See Glasstone (20)). The value of a_m thus defined would closely approximate the arithmetic mean if a_1 and a_2 did not differ too widely. The discrepancy amounts to only about 10 percent, for example, if $a_1/a_2 = 4$. Similar remarks apply to the coefficient b_m.

Adsorption values were calculated from the Gibbs adsorption equation for single components and for each component from the mixtures. These values are given in Tables 4 and 5 and in Figures 20 and 21. Theoretical adsorption isotherms can be calculated from the theoretical equations. Since $KT\Gamma = p\frac{d\pi}{dp}$ for single component adsorption and $KT\Gamma_1 = p_1\frac{\partial\pi}{\partial p_1}$ in the case of mixed adsorption, an expression for the derivatives may be found from the experimental equations and equated to $KT\Gamma$. The adsorption can then be calculated by substituting values for π , the constants, and the calculated p values. Thus from equation 14

Table 4. Adsorption of n-Heptane on Mercury at 30° C

p_E = 0	
p_H(mmHg)	Γ_H(molecules/cm^2)
4.2	1.5 x 10^{14}
6.3	1.8
10.0	2.3
13.1	2.5
15.9	2.6
17.7	2.7
20.0	2.8
25.1	3.1
27.5	3.3
32.7	3.6
40.2	4.6
47.4	5.5

p_E = 11.5 mm	
p_H(mmHg)	Γ_H(molecules/cm^2)
9.2	1.8 x 10^{14}
16.8	2.3
29.3	3.3
34.5	3.8
44.6	4.8
57.4	6.7

p_E = 27.5 mm	
p_H(mmHg)	Γ_H(molecules/cm^2)
5.0	1.1 x 10^{14}
7.5	1.1
10.0	1.2
14.6	1.2
20.0	1.3
25.5	1.6
30.0	2.3
35.0	2.7
41.7	3.6
45.0	4.2
50.0	5.2

p_E = 41.2 mm	
p_H(mmHg)	Γ_H(molecules/cm^2)
6.0	1.1 x 10^{14}
7.5	1.3
10.0	1.6
12.5	1.7
15.0	1.7
20.0	1.2
25.0	0.8
30.0	0.6
35.0	0.4

Table 5. Adsorption of Ethanol on Mercury at 30° C

$p_H = 0$	
p_E(mmHg)	Γ_E(molecules/cm^2)
2.2	2.1×10^{14}
6.7	2.5
9.4	2.7
12.6	3.1
16.9	3.4
25.1	3.8
31.6	4.2
45.0	5.3
50.1	5.7
60.8	6.5

$p_H = 10$ mm	
p_E(mmHg)	Γ_E(molecules/cm^2)
11.5	0.4×10^{14}
20.0	1.1
27.5	2.3
35.0	5.1
37.5	6.2
39.8	7.5

$p_H = 20$ mm	
p_E(mmHg)	Γ_E(molecules/cm^2)
11.5	0.4×10^{14}
20.0	0.9
27.5	2.1
35.0	5.1
37.5	6.3
39.8	7.2

$p_H = 40$ mm	
p_E(mmHg)	Γ_E(molecules/cm^2)
11.5	0.1×10^{14}
20.0	0.1
27.5	0.3
31.6	1.3
35.0	2.6
37.5	3.7
39.8	4.8

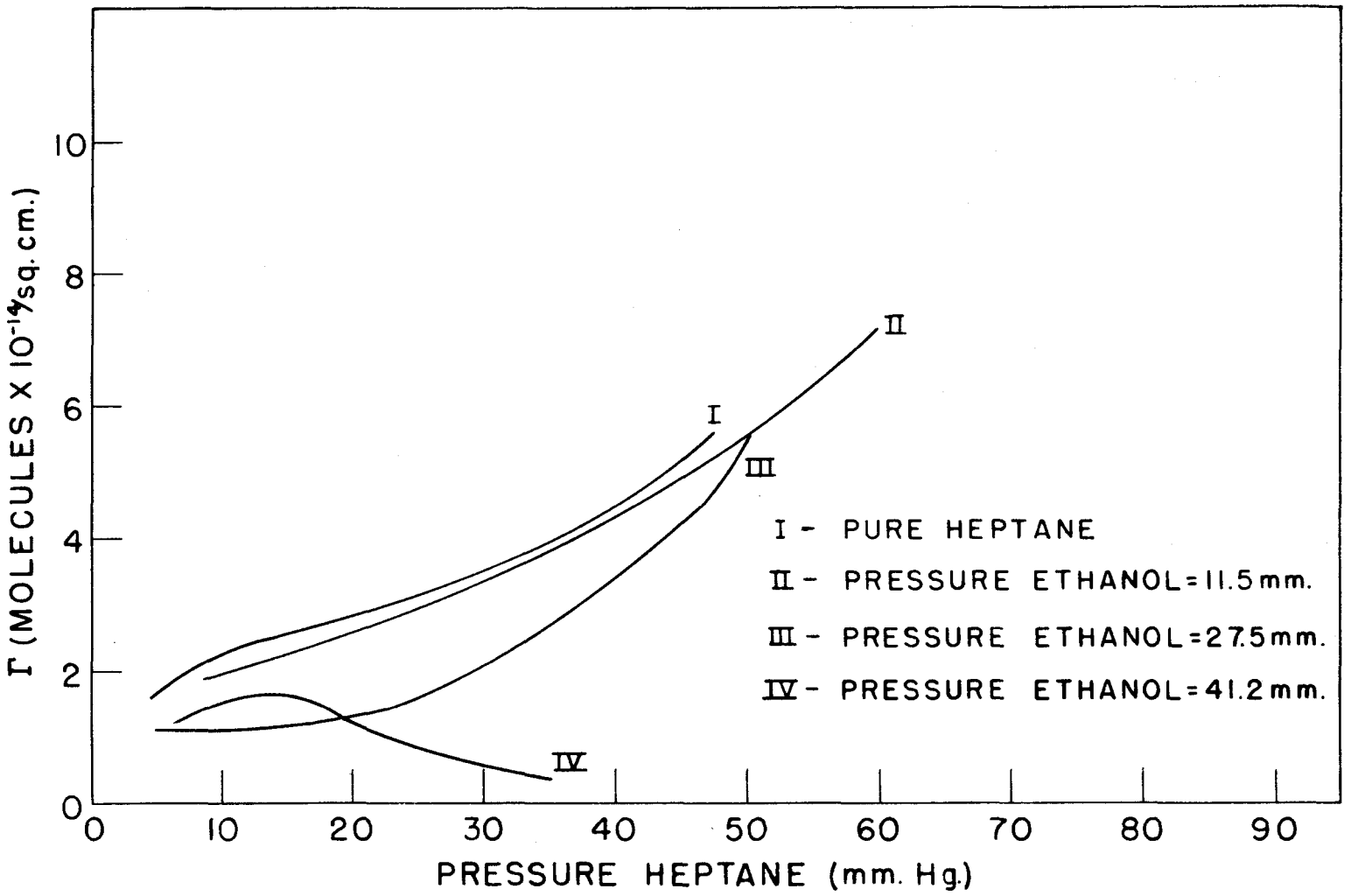

FIGURE 20. ADSORPTION OF n-HEPTANE CALCULATED FROM EXPERIMENTAL DATA FOR HEPTANE AND HEPTANE-ETHANOL MIXTURES AT 30° C

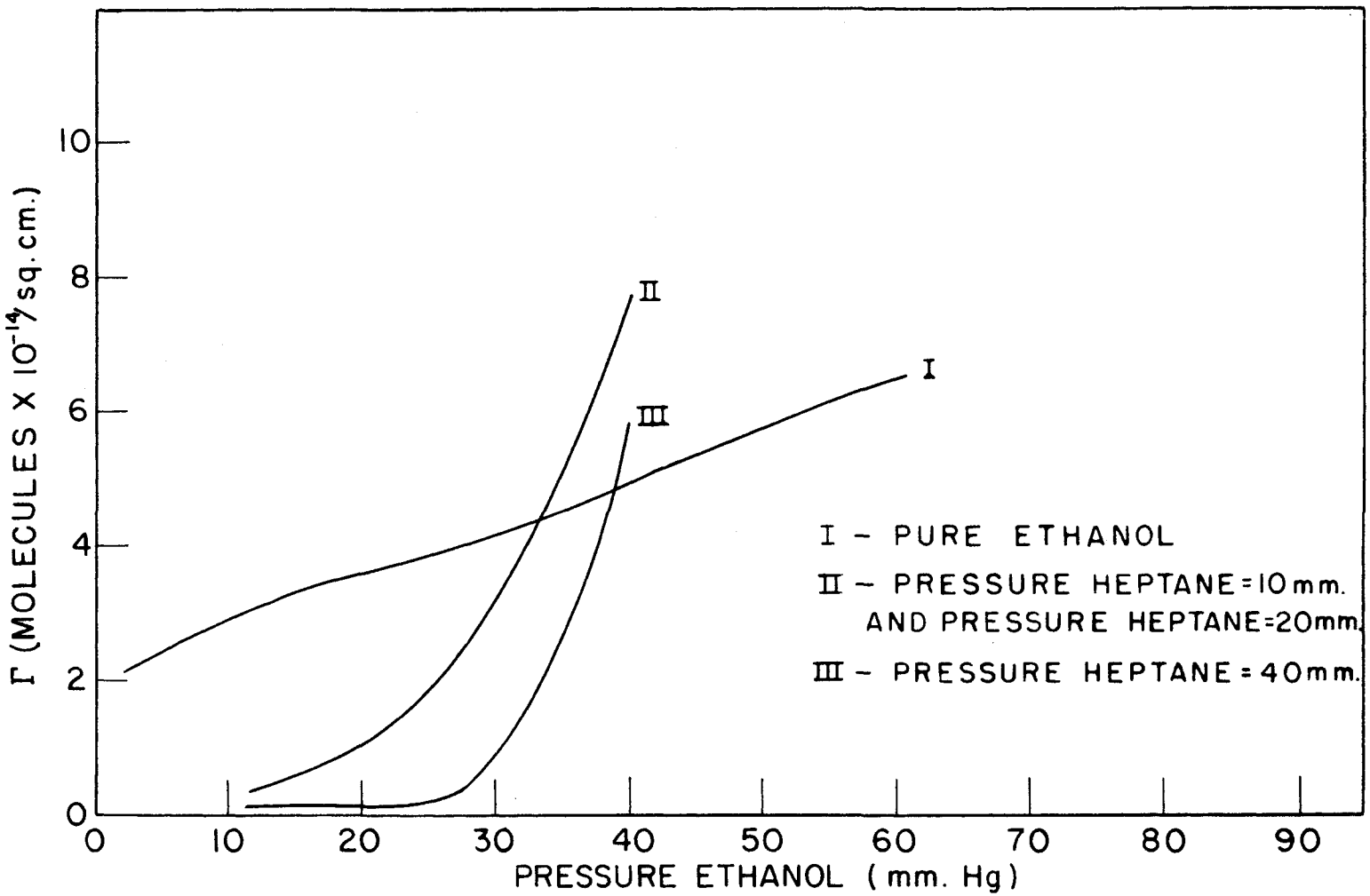

FIGURE 21. ADSORPTION OF ETHANOL CALCULATED FROM EXPERIMENTAL DATA FOR ETHANOL AND n-HEPTANE - ETHANOL MIXTURES AT 30°C

$$KT\Gamma_1 = \frac{c_1 p_1 10^{-a_1\pi + b_1\pi^2}}{1 + c_1 p_1(\alpha_1 - 2\beta_1\pi)10^{-a_1\pi + b_1\pi^2} + c_2 p_2(\alpha_2 - 2\beta_2\pi)10^{-a_2\pi + b_2\pi^2}}$$

($\alpha = 2.303a$; $\beta = 2.303\ b$). Three theoretical adsorption curves are given in Figure 22. Curve I was calculated for pure heptane from the above equation. It agrees well with the experimental adsorption isotherm in Figure 20. Curve II was also calculated from the above equation. It represents the adsorption of heptane from the mixture in which the pressure of ethanol was 11.5 mm. This theoretical curve agrees well with the experimental values at low pressures, but not so well at the higher pressures. Since the surface pressure-pressure curve deviates from the experimental values at high pressures this is to be expected. Curve III was calculated from equation 12. It represents theoretical adsorption of heptane from the mixture in which the ethanol pressure was 41.2 mm. It seems likely that this represents the adsorption better than that calculated from the experimental data. It was difficult to decide how a curve should be drawn through the experimental points in this case and it certainly seems more likely that beyond a pressure of 15 mm the adsorption of heptane remains constant or increases only slightly with increasing pressure than that the adsorption decreases as indicated from the experimental results. Comparisons of Figures 14 and 17, of 15 and 18, and of 16 and 19 indicate the following: (1) the equation containing the interaction term represents heptane adsorption better than the one which does not contain this term, (2) the two equations fit the ethanol data about equally well, and (3) while the interaction equation fits the

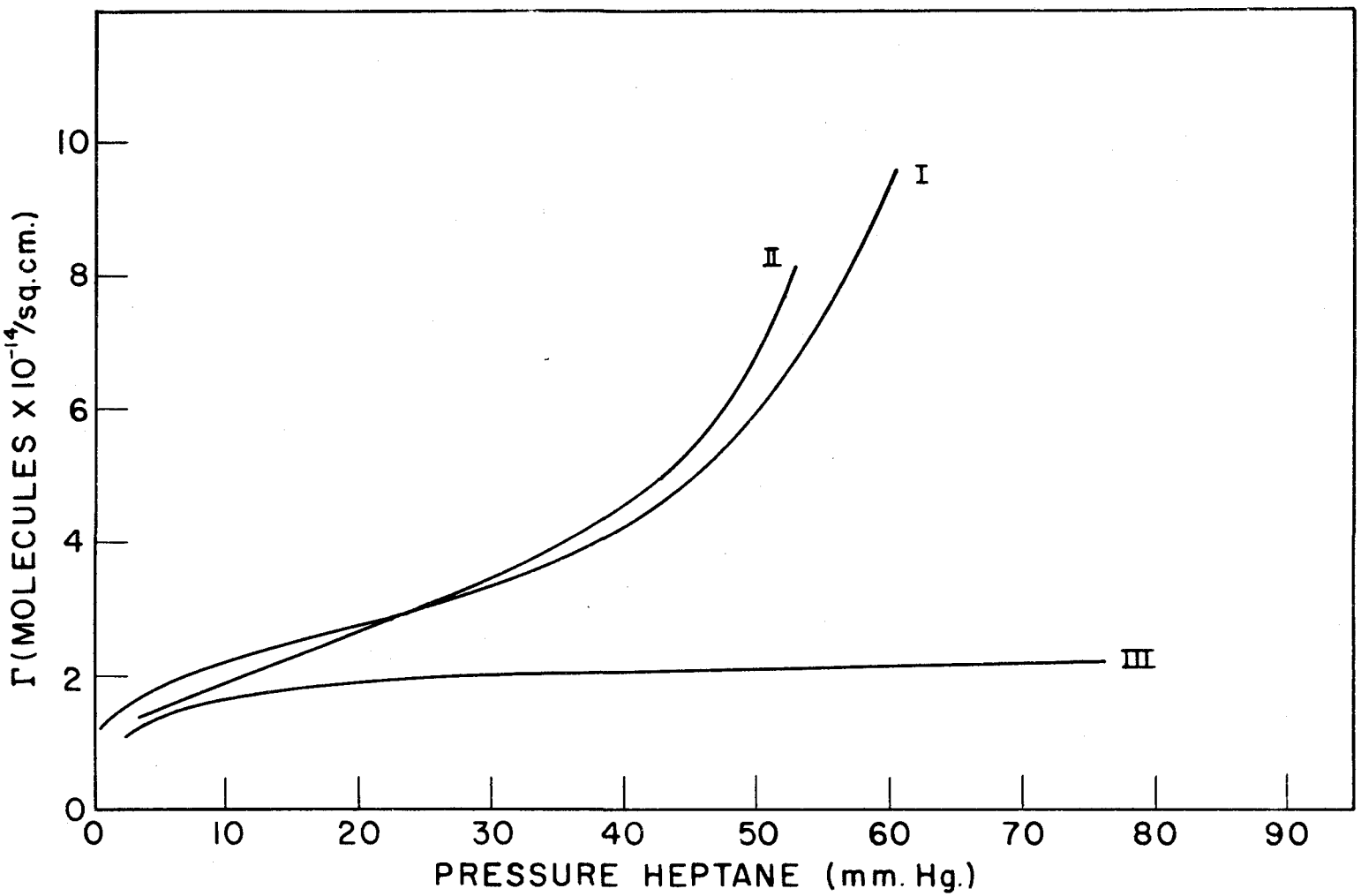

FIGURE 22. ADSORPTION OF HEPTANE CALCULATED FROM THEORETICAL EQUATIONS

mixture composed of the least amount of ethanol somewhat better than does the other equation, this non-interaction equation fits the data for the other two mixed systems considerably better than does the interaction equation.

One could feel much more confident about all of these results if the mercury had been pure. Since the ethanol adsorption was apparently hindered by the presence of whatever impurity was present, this unknown quantity undoubtedly had some effect upon the course of adsorption from mixed vapors. Another factor which may complicate the mixture is the possibility of condensed films or multimolecular adsorption. Kemball and Rideal (24) found that above a pressure of about 20 mm heptane formed either a condensed film or a second layer. If one assumes that the heptane molecules are partially curled up on the surface with an area of 30-35 A^2, then a monolayer would be completed at approximately this pressure according to the calculated adsorption. If the molecules were standing on end with an area of 20 A^2, a monolayer would still be completed at a pressure of 45 mm or less. Hence it appears likely that there is multimolecular adsorption of heptane at higher pressures. This could explain the failure of the Volmer equation to explain heptane adsorption at the higher pressures.

Kemball (26) also found that ethanol formed a second layer at a surface pressure of 39 dynes/cm which corresponded to 5 or 6 mm vapor pressure in his case. Adsorption calculations from these data indicate completion of a monolayer at approximately the same surface

pressure although the vapor pressure is considerably higher. Adsorption calculations for mixed adsorption indicate similar results except for the case of the highest ethanol pressure (41.2 mm). In this latter case the heptane monolayer seems to be incomplete but the ethanol seems to be adsorbed to a greater extent than a monolayer, perhaps a layer on top of a layer of heptane. It is not surprising then that the interaction equation which seems to explain single adsorption so well should fail to account adequately for the mixed adsorption case. The constants in this equation apparently can be adjusted so as to fit a single adsorption isotherm even though multimolecular adsorption may be involved. It may be that this causes an overcorrection in the case of mixed adsorption. It may be fortuitous that the Volmer type equation explains the mixed adsorption as well as it does or it may be that since it is good for only the monolayer it explains mixed adsorption up to the point where multimolecular adsorption sets in. The interaction equation predicts greater adsorption than is observed. Perhaps there is additional interaction between the unlike molecules for which this equation fails to account. Additional data must be obtained before much more can be said about the adsorption of these vapors on mercury.

The work that has been done with the apparatus indicates that it can well be used to study the adsorption of various vapors and of various mixtures of vapors on mercury. Additional efforts to further purify the mercury need to be made first, of course.

With suitable modifications the usefulness of the apparatus can

be extended. A study of the adsorption of permanent gases would be one of the simplest extensions. The gas to be studied, after being purified and dried, could be introduced into the system through the valve as the vapor was in this work.

It should be possible without too much difficulty to freeze a drop of mercury and photograph the frozen drop. This would indicate the validity of the method of determining surface tension by measuring solidified drops of other metals (See page 16).

Interfacial tensions of liquids and mercury could be made if suitable modifications were made to permit the introduction of liquid. It might also be possible to study adsorption from solution with this method.

VI. SUMMARY

1. A pendent drop apparatus for the measurement of surface tension of mercury and similar substances in high vacuum under conditions of maximum purity was designed, built, and demonstrated to be practical. Provisions for the admission of one or more vapors of high purity to desired partial pressures were incorporated. Suggestions for improvement of the apparatus and for possible extensions of its usefulness were made.

2. The surface tension of purified mercury was found to be 460 ± 2 dynes/cm at 30° C. This value was reproduced under a variety of experimental conditions and purification procedures. The presently accepted value is about 25 dynes/cm higher than this. Since even small amounts of impurities lower the surface tension of mercury, the most probable explanation for this discrepancy is that, despite the precautions exercised, the purity of the mercury used in this work was not entirely satisfactory.

3. The dependence of surface tension lowering of mercury on the partial vapor pressure of n-heptane and of ethanol, both as pure components and from mixtures of the two vapors, was experimentally observed at 30° C. From these data adsorption isotherms were inferred.

4. An equation of state of approximately virial form was found to represent adsorption of the single components quite well. Such an equation of state represented adsorption from mixtures less well. The significance of these results with respect to molecular interactions was discussed.

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